




3 1761 06705749 7

UNIV. OF
TORONTO
LIBRARY

BINDING LIST DEC 1 1922



Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

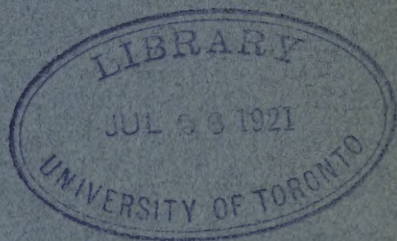
LELAND STANFORD JUNIOR UNIVERSITY PUBLICATIONS
UNIVERSITY SERIES

The Electrical Charges of Atoms and Ions

BY

FERNANDO SANFORD

Professor of Physics



STANFORD UNIVERSITY, CALIFORNIA
PUBLISHED BY THE UNIVERSITY
1919

UNIVERSITY SERIES

- INHERITANCE IN SILK WORMS, I. Vernon Lyman Kellogg, Professor of Entomology. 89 pp., 4 plates. 1908. Price \$1.00.
- THE OPISTHOBRANCHIATE MOLLUSCA OF THE BRANNER-AGASSIZ EXPEDITION TO BRAZIL. Frank Mace McFarland, Professor of Histology. 105 pp., 19 plates. 1909. Price \$1.00.
- A STUDY OF THE NORMAL CONSTITUENTS OF THE POTABLE WATER OF THE SAN FRANCISCO PENINSULA. John Pearce Mitchell, Assistant Professor of Chemistry. 70 pp., 1 map. 1910. Price 50c.
- SYNOPSIS OF THE TRUE CRABS (BRACHYURA) OF MONTEREY BAY, CALIFORNIA. Frank Walter Weymouth. 64 pp., 14 plates. 1910. Price 50c.
- THE OSTEOLGY OF CERTAIN SCOMBROID FISHES. Edwin Chapin Starks, Assistant Professor of Zoology. 49 pp., 2 plates, 1 text figure. 1911. Price 50c.
- A PHYSICAL THEORY OF ELECTRIFICATION. Fernando Sanford, Professor of Physics. 69 pp., 2 plates. 1911. Price 50c.
- THE MATZKE MEMORIAL VOLUME. Papers by John Ernst Matzke, late Professor of Romanic Languages, and Thirteen Colleagues. 162 pp. 1911. Price \$1.00.
- DAS HISTORISCHE PRÄSENS IN DER ÄLTEREN DEUTSCHEN SPRACHE. Bruno Boezinger, Assistant Professor of Germanic Languages. 91 pp. 1912. Price 50c.
- THE EFFECT OF A STRICTLY VEGETABLE DIET ON THE SPONTANEOUS ACTIVITY, THE RATE OF GROWTH, AND THE LONGEVITY OF THE ALBINO RAT. James Rollin Slonaker, Assistant Professor of Physiology. 36 pp., 1 plate, 15 text figures. 1912. Price 50c.
- CATALOGUE DE TOUS LES LIVRES DE FEU M. CHAPELAIN. (Bibliothèque Nationale, Fonds Français, Nouv. Acq., No. 318.) Colbert Searles, Associate Professor of Romanic Languages. 119 pp., 2 plates. 1912. Price 75c.
- THE DUDLEY MEMORIAL VOLUME. Papers by William Russell Dudley, late Professor of Botany, and Several Colleagues. 137 pp., 12 text figures, 9 plates. 1913. Price \$1.00.
- THE FISHES OF THE STANFORD EXPEDITION TO BRAZIL. Edwin Chapin Starks, Assistant Professor of Zoology. 77 pp., 15 plates. 1913. Price 75c.
- THE BIRDS OF THE LATIN POETS. Ernest Whitney Martin, Associate Professor of Greek. 260 pp. 1914. Price \$1.00.
- ACCELERATION IN THE DEVELOPMENT OF THE FOSSIL CEPHALOPODA. James Perrin Smith, Professor of Paleontology. 30 pp., 15 plates. 1914. Price 75c.
- A MORPHOLOGICAL STUDY OF SOME MEMBERS OF THE GENUS PALLAVICINIA. Douglas Houghton Campbell, Professor of Botany, and Florence Williams. 44 pp., 23 text figures. 1914. Price 50c.
- THE EVOLUTION OF BRAZIL COMPARED WITH THAT OF SPANISH AND ANGLO-SAXON AMERICA. Manuel de Oliveira Lima, Minister of Brazil to Belgium. 160 pp. 1914. Price \$1.00.
- THE HEMOLYMPH NODES OF THE SHEEP. Arthur William Meyer, Professor of Anatomy. 74 pp., 1 plate, 4 colored plates. 1914. Price \$1.00.
- AN INTRODUCTION TO THE STUDY OF THE ENDOCRINE GLANDS AND INTERNAL SECRETIONS. (Lane Medical Lectures.) Sir Edward Schäfer, Regius Professor of Physiology in the University of Edinburgh. 94 pp., 1914. Price 75c.

(Continued on third page of cover.)

Physics
Elect
3

LELAND STANFORD JUNIOR UNIVERSITY PUBLICATIONS
UNIVERSITY SERIES

The Electrical Charges of Atoms and Ions

BY

FERNANDO SANFORD

Professor of Physics



177/30
27/12/22

STANFORD UNIVERSITY, CALIFORNIA
PUBLISHED BY THE UNIVERSITY
1919



STANFORD UNIVERSITY
PRESS

CONTENTS

| | PAGE |
|--|------|
| INTRODUCTION | 5 |
| ELECTROLYTIC DISSOCIATION AND THE CHARGES OF IONS | 9 |
| Theory of Electrolytic Dissociation | 9 |
| Ionic Mobility and Ionic Charges | 14 |
| Computation of Ionic Charges | 19 |
| Ionic Charges and Cohesion | 20 |
| Cohesion Between Ions and Water | 25 |
| Cohesion of Compound Molecules | 27 |
| Ionic Charges and Boiling Points | 28 |
| Molecular Charges and Boiling Points | 30 |
| Vapor Pressure of Ammonia of Crystallization as Related to the Negative Ion of the Molecule | 30 |
| Critical Temperature and Ionic Charges | 32 |
| Molecular Charges and Critical Temperatures | 32 |
| Atomic Heat of Fusion and Ionic Charge | 33 |
| Ionic Charges and Surface Tension | 34 |
| Influence of the Ionic Charges of the Alkali Metals upon the Sur- face Tension of Mercury in which the Metals are Dissolved | 34 |
| Relation of Specific Gravity to Ionic Charges | 35 |
| Relation of Ionic Charges to Heats of Formation | 36 |
| Relation of Molecular Heat of Formation to the Resultant Molecular Charge | 39 |
| Ionization of Gases and Ionic Charges | 40 |
| Heat of Ionization and Ionic Charges | 42 |
| Molecular Charges and Solubility | 43 |
| Influence of the Molecular Charge of the Solvent upon the Solubility of a given Substance | 44 |
| Expansion of Salts in Water Solution Compared with their Resultant Molecular Charges | 46 |
| Atomic Charges and Serial Numbers of the Elements | 47 |
| Charges of Ions from Hot Metals | 54 |
| Mobilities of Positive Ions in Flames | 57 |

| | PAGE |
|---|------|
| POSITIVE ATOMIC CHARGES AND RADIATION | 59 |
| On the Nature of Electromagnetic Radiation | 59 |
| On the Elementary Charge of Hydrogen | 64 |
| Positive Atomic Charges and X-Rays | 71 |
| Orbital Velocity of Electrons which produce X-Rays | 78 |
| Relation of the Nuclear Charge in Radiation to Ionic Charges in Electrolysis | 80 |
| CHARACTERISTIC CHARGES OF METALS IN THE SOLID STATE | 83 |
| THE ELECTRICAL CHARGE OF THE EARTH | 94 |
| CHARACTERISTIC CHARGES AND SPECIFIC INDUCTIVE CAPACITY OF METALS | 102 |
| Influence of Temperature upon the Specific Inductive Capacity of Metals | 110 |
| Specific Inductive Capacity and the Voltaic Cell | 112 |
| THEORETICAL CONSIDERATIONS | 115 |
| LIST OF TABLES | 129 |
| LIST OF FIGURES | 130 |

INTRODUCTION

The first attempts to explain chemical reactions by means of electrical forces date from the end of the eighteenth century, and were suggested principally by the phenomena of electrolysis. Previous to Volta's discovery of the electrical current, however, i. e., in the year 1789, Bennett published the first experiments on the electrification of two metals by contact with each other. He found that two pieces of unlike metal, after being freed from electrical charges by contact with an earthed conductor, were capable of giving opposite charges to each other when insulated and placed in contact. He gave the title "Experiments on the Adhesive Electricity of Metals and Other Conducting Substances" to his investigations and concluded that different metals have different affinities or different adhesive forces for the electrical fluid.

Six years later (in 1795) Cavallo published the results of a series of experiments on contact electrification, as a result of which he says:

I am inclined to suspect that different bodies have different capacities for holding the electric fluid, as they have for holding the elementary heat.

Meantime (in 1791) Galvani had discovered the twitching of a frog's muscles due to electrical stimulation, and Fabroni had written (in 1792) his paper entitled "Upon the Chemical Working of the Different Metals Upon Each Other at Ordinary Air Temperatures and Upon the Explanation of Certain Galvanic Phenomena". In this paper Fabroni describes a number of experiments to show that when two pieces of different metal are placed in contact, either in air or in water, one of the metals frequently becomes more oxidizable than it was while separated from the other metal. He says:

Since the metals have relationships with each other, the molecules must mutually attract each other as soon as they come into contact. One cannot determine the force of this attraction, but I believe it to be sufficient to weaken their cohesion so that they become inclined to go into new combinations and to more easily yield to the influence of the weakest solvents.

Fabroni showed that when in contact with the nobler metals the more oxidizable metals may even dissolve in water and, in some cases, form salts which may crystallize out.

Since the conditions under which contact electrical charges were produced were the same as those which were observed by Fabroni to render his metals more oxidizable and were the same as those under which Galvani was able to produce the contractions in the muscle of a frog, Fabroni concluded that the electrical effects in the two cases were the

results of chemical action which had been made possible by the contact of the unlike metals.

The question whether the transference of an electrical charge from one metal to another when the two are insulated and brought into contact is a primary phenomenon or is due to a chemical change brought about in the metals on account of this contact is one which has divided the physicists and chemists of the past century into two contending groups, and has given rise to a large part of the controversial writing in physics for one hundred years. In this controversy Fabroni has usually been regarded as the founder of the chemical theory of contact electrification; but his followers have generally failed to recall that Fabroni regarded the weakening of cohesion in the more oxidizable metal, or, as we now say, the more electropositive metal, as a condition precedent to chemical action. With our present understanding of the relation between electrical charges and cohesion it seems more than probable that Bennett and Fabroni were both observing the same phenomenon from different view-points. Bennett observed that certain metals when in contact with nobler metals became positively electrified; Fabroni observed that under the same condition these metals have their cohesion weakened and become more oxidizable.

With the discovery of electrolysis by Nicholson and Carlisle, in 1800, a new view-point for observing the relation between cohesion and electrical phenomena was gained. In the passage of an electric current through a liquid solution it was found that the solution was always separated into at least two constituents, and that one of these constituents appeared at the positive pole of the battery and the other at the negative pole. The most natural inference to be drawn from this phenomenon was that one of the constituents was positively electrified and the other was negatively electrified, and that it was by virtue of their electrical charges that they were drawn to the poles of the battery. The two leading chemists of that day, Davy and Berzelius, adopted this hypothesis, and the classification of the constituents of electrolytes into electropositive and electronegative soon led to the application of the same terms to the atoms of elementary substances.

While Davy and Berzelius agreed as to the electrical nature of the forces by which the atoms of different elements are held together in their compounds, they differed as to the origin of these electrical forces. Davy was impressed by the fact that elementary substances which may combine with each other become oppositely electrified upon contact with each other when insulated, and he concluded that it was these opposite charges which were induced by contact that were the cause of the attraction known as chemical affinity. It would seem to follow from this hypothesis that these

electrified constituents of the chemical molecule may again be separated by electrical forces stronger than their own affinity, and that under these circumstances the positive constituents may go to the negative pole and the negative constituents to the positive pole of the battery which furnishes the separating force.

Berzelius, on the other hand, maintained that the atoms of elementary substances were in and of themselves electrified, and that they carried charges which were characteristic of all the atoms of each particular element. He believed that each atom carried both positive and negative charges which were not capable of combining so as to neutralize either, and that these charges were not concentrically arranged in the atom, hence that each atom must possess an "electric polarity" analogous to the magnetic polarity in the smallest particles of a magnet. In an outline of his theory in volume 34 of *Nicholson's Journal*, Berzelius says:

Admitting that bodies consist of particles or atoms placed near each other, in such manner as may appear from their property of combining in proportions of their multiples, we may consider these atoms as possessing an electric polarity upon the intensity of which the force of their affinity depends. In this case the chemical affinity becomes identified with electricity, or rather the electric polarity. In order to explain the different electro-chemical characters, we must add to the general polarity a kind of specific unipolarity, by means of which one of the poles contains more of the $+E$, or of the $-E$, than the opposite electricity in the other pole is capable of saturating. A body of which the positive pole predominates, that is, which contains an excess of positive electricity, constitutes an electro-positive body, and *vice versa*.

* * * * *

As we know from fact and experience, that bodies of the same electro-chemical class (that is to say, bodies in which we conceive that the same pole predominates) can combine, it appears that the force of affinity depends rather on the intensity of the general polarity, than of the specific unipolarity; and from this reason it may be that sulphur has more affinity with oxygen than gold or platina has, although sulphur has the same unipolarity as oxygen, and those metals have an opposite polarity to that of oxygen.

Berzelius arranged the known elements in an electrical series beginning with oxygen, which he called the absolutely electro-negative element, because in the electrolysis of all its compounds it seeks the positive pole, and ending with potassium, as the most strongly electro-positive element.¹

To the present writer, the theory of Berzelius seems to be much more nearly in accord with our present understanding of the facts than does the theory of Davy, or of any other chemist since Berzelius. We now know that the chemical atoms with which Berzelius was at that time concerned are, at least in most cases, made up of particles which are in and of themselves electropositive or electronegative. Since it is extremely

¹ Rubidium and caesium were not then known.

improbable that these electric particles are all concentrically arranged in the atom, it follows that an atom must have an external electric field which is not uniform over the surface of the atom. Thus an atom must have at least two electrical poles.

That either the positive or negative charge is usually in excess in atoms will be shown in many ways in the following pages. That affinity and cohesion are merely the results of the mutual attractions of the resultant atomic and molecular charges will also be shown more fully.

There are at least four possible means of studying the electrical relations between the constituents of the chemical atom. These are electrolytic dissociation, ionization by means of heat, by ultra-violet light and by X-rays, radioactive transformations, and the various sorts of electromagnetic radiation sent off by atoms and molecules. The present paper will deal principally with the phenomena of electrolysis and with radiation phenomena, but the bearings of radioactivity and of other forms of ionization will necessarily receive some consideration.

In addition to the phenomena included under the above heads it is possible to find numerous relations between the electrical properties of bodies and the forces known as cohesion and chemical affinity, and some of these relations are important to any discussion of atomic charges. Likewise, the part played by specific inductive capacity is fundamental and must necessarily be recognized in a discussion of this character.

ELECTROLYTIC DISSOCIATION AND THE CHARGES OF IONS

Theory of Electrolytic Dissociation

After Davy and Berzelius, the next great advances in the knowledge of electrolytic phenomena were due to Faraday. Faraday had been trained in Davy's laboratory, and very naturally followed up many of the lines of work which Davy had begun.

One of the first questions investigated by Faraday was that of the method of chemical decomposition by the current. His earlier views on the subject seemed to differ materially from those held by Davy and Berzelius as well as from those which he, himself, held later. In "Experimental Researches," 1, paragraphs 518-519, he says:

Passing to the consideration of electro-chemical decomposition, it appears to me that the effect is produced by an *internal corpuscular action*, exerted according to the direction of the electric current, and that it is due to a force either *super-added to*, or *giving direction to the ordinary chemical affinity* of the bodies present. The body under decomposition may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current in one direction parallel to the course of the latter, and strengthened or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses.

In this view the effect is considered as *essentially dependent* upon the *mutual chemical affinity* of the particles of opposite kinds.

Faraday then continues to argue that the dissociated particles of the electrolytic compound, which he later names ions, move through the solution under the impulse of chemical affinity alone, and that they are set free at the poles only on account of their chemical affinity for the metal of the pole. The sole effect of the current is to make the chemical affinity greater in one direction than in any other. Whether this is done by an orientation of the ions, or otherwise, Faraday does not say. In this view, the opposite charges of the poles of the battery are not assumed to play any part, and apparently there is no recognition of the opposite electrification of the two constituents into which the compound is separated.

Later, Faraday came to recognize the identity of affinity and electric attraction. After he had proved that an equal quantity of any given electrolyte is decomposed by any cross section of a given current, and that chemically equivalent quantities of different substances are decomposed by the same current, he concluded that the quantity of

substance decomposed could be used as the measure of the total quantity of electricity which had passed through the solution. He then says (paragraph 855) :

Considering this close and twofold relation, namely, that without decomposition transmission of electricity does not occur; and, that for a given definite quantity of electricity passed, an equally definite and constant quantity of water or other matter is decomposed; considering also that the agent, which is electricity, is simply employed in overcoming electrical powers in the body subjected to its action; it seems a probable, and almost a natural consequence, that the quantity which passes is the *equivalent* of, and therefore equal to, that of the particles separated; i. e., that if the electrical power which holds the elements of a grain of water in combination, or which makes a grain of oxygen and hydrogen in the right proportions unite into water when they are made to combine, could be thrown into the condition of a *current*, it would exactly equal the current required for the separation of that grain of water into its elements again.

Faraday accordingly concludes that an electric current in an electrolyte is accompanied by the movement in opposite directions of positively and negatively charged ions. Even at this stage of his theory he seems not to recognize that the movement of these charged particles actually *constitutes* the electrical current. The question as to what becomes of the charges on these ions when they escape at the electrodes is also not considered at this time. There was at that time a question at issue between Grotthuss and De la Rive as to whether the ions take up neutralizing charges from the electrodes when they escape as gases, or whether they give off to the electrodes the surplus charges which they carry. In Faraday's electrical theory this question could hardly be said to arise, because Faraday's theory did not necessarily involve the existence of any electric fluid or substance whatever. Later, Faraday seems to have decided in favor of the De la Rive hypothesis that the ions part with their charges to the electrodes. Thus in paragraph 1622-24 he describes an experiment in which a current was made to flow around a circuit containing both an electrolytic resistance and an air gap, and in conclusion he says :

So when a particle of air, or dust in it, electrified at a negative point, moves on through the influence of the inductive forces to the next positive surface, and after discharging passes away, it seems to me to represent exactly that particle of oxygen which, having been rendered negative in the electrolyte, is urged by the same disposition of inductive forces, and going to the positive platina electrode, is there discharged, and then passes away, as the air or dust did before it.

Thus, as a final result of his work, Faraday concludes that the ions which move through the liquid in electrolysis actually carry electric charges which they part with at the electrodes, and that these moving charges actually constitute the electrical current. Then, since he was able to show that a definite quantity of electricity (96470 coulombs) must be

passed through any electrolytic conductor in order that a gram-atom of any monovalent element may be liberated at one of the electrodes, and since a gram-atom of any element contains the same number of chemical atoms, he was led to the conclusion that each atom of any monovalent element and each monovalent ion, whether simple or compound, must carry the same charge, and that multivalent ions must carry simple multiples of this charge.

This hypothesis of Faraday's as to the equality of charges on monovalent ions has come to be a part of the standard electrochemical theory of our text-books. Thus Arrhenius, in his "Text-Book of Electrochemistry," after discussing Faraday's second law, says:

The simplest conception which can be derived from this law is that the gram-equivalent of every ion carries a charge of 96,500 coulombs, and consequently all equivalents have the same charge. When the electricity passes through a liquid it is transported by the ions, the positive electricity being carried by the positive ions and the negative by the negative ions. The electricity is firmly bound to the ions, and can only be given up at the electrodes, and the ions then cease to exist as such. It is easy to understand that equivalent quantities of different substances are charged with the same amount of electricity; for when we mix solutions of two electrolytes—for instance, calcium chloride (CaCl_2) and sodium nitrate (NaNO_3), partial exchange takes place, and there are formed sodium chloride (NaCl) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$). Now, if one atom of calcium (=2 equivalents) were not charged with the same quantity of electricity as two NO_3 radicles, or the two sodium atoms originally combined with these, but had a greater positive charge, the molecules of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) would be positively charged, and the sodium chloride molecules would be negatively charged, since the original solutions were electrically neutral. By evaporation or by some chemical means, one kind of molecule, *e. g.* the sodium chloride molecules, can be precipitated from the solution, or the two substances can be separated by diffusion. After this separation the solutions should be electrically charged. As not the slightest charge can be found on the solutions, we must assume that equivalent quantities of the various substances have the same charge.

Thus we see that the equality of charges on electrolytic ions of equal valency has become a tenet of our standard electrochemical theory, though it was founded upon a concept of the nature of electrolysis which is no longer held. One of the fundamental assumptions upon which this doctrine was originally based is that there are two kinds of electricity which may be imparted to chemical atoms, and which may again be given up by the atoms. One of these kinds is carried by the anions and the other kind by the cations. Both kinds of ions may give up their charges to the electrodes and become again uncharged atoms.

We now believe that no electric charge, as such, is given to either electrode in electrolysis. In the ordinary forms of voltaic cells one electrode goes into solution in the form of positive ions, consisting, apparently, of the chemical atoms of the metal minus one, or, possibly, more, electrons.

At the other electrode similar positive sub-atoms (the cations) go out of the solution and combine with the electrode, or, after taking up electrons from the electrode combine with other positive sub-atoms and escape as ordinary gas molecules. The ions which are in the electrolytic solution at the beginning of the process are apparently the electropositive and electro-negative constituents of the electrolyte, which, on account of the weakening of their electrical attraction for each other by the high specific inductive capacity of the solvent, are constantly breaking apart and recombining. In the common voltaic cell the same negative ions remain in the solution during the whole electrolytic process, and these ions neither receive nor give off any electric charges whatever. They merely combine with other ions, or dissociate from other ions. The only changes which take place in the electrolytic solution are due to positive ions which escape into the solution from the more soluble metal and to the loss of positive ions which escape from the solution at the surface of the less soluble metal; or, in other words, positive ions escape from the metal in which cohesion is weaker and are deposited upon the metal in which cohesion is stronger.

In the case of a cell consisting of zinc and copper plates and a solution of copper sulphate, for example, the process seems to be as follows: When the copper and zinc plates are put into the copper sulphate solution both begin to exchange some of their own metallic ions for metallic ions already in the solution. If the zinc plate be put into the solution alone, its ions will gradually go into solution and will be replaced by the copper ions in the solution. The same exchange takes place, though more slowly, in the case of the copper plate. That is, exchanges are continually taking place between the ions of the solution and the surface ions of the copper. In the case of the zinc plate, the replacement of its ions by copper ions will continue until the zinc is all dissolved or until the copper ions of the solution are all deposited.

Since only the positive sub-atoms of the zinc go into the solution to form ions, they must leave some of the electrons which were previously associated with them in the metal plate. During the process of solution the zinc plate is accordingly becoming negatively electrified, since it is acquiring an excess of negative electrons. If no electropositive ions were deposited upon it from the solution, the plate would finally become so strongly electronegative that it would hold back its positive ions and prevent their further escape into the solution. This occurs when the zinc is placed in a dilute solution of sulphuric acid from which it can acquire no electropositive metallic ions, the hydrogen ions which are set free at its surface escaping from the solution in the form of hydrogen gas.

It will be seen that this process tends to make the solution more

electropositive at the same time that it makes the metal electronegative. Both of these changes tend to hinder the further escape of positive ions from the metal into the solution. If the metal be earthed, so that its negative electrons may escape as fast as they are set free by the solution of its positive ions, the metal will continue to dissolve until the solution becomes sufficiently electropositive to prevent more positive ions from entering it. If the metal be then withdrawn, the positive charge of the solution may be measured by an electrometer.

On the other hand, if there were an infinite quantity of the solution, so that its positive charge could never become appreciable, the ions would continue to escape from the metal until its negative charge became sufficient to hold them back. In this case, the, so-called, single potential difference between the metal and the solution would be entirely due to the charge on the metal. In the former case it would be due to the charge in the liquid. Usually it is due to the algebraic difference of these charges.

When two metals, as zinc and copper, are put into the same solution, since zinc ions escape into the solution faster than copper ions, the zinc plate requires a stronger negative charge to enable it to hold its positive ions from escaping than does the copper plate. Or, if we speak in terms of cohesion or affinity, the cohesion of the copper plate for the positive sub-atoms on its surface is stronger than the cohesion of the zinc plate for its corresponding electropositive sub-atoms. When both zinc and copper plates are in the same electrolytic solution and are joined by a conducting wire, the zinc plate cannot remain appreciably more electronegative than the copper plate. Accordingly, since the potential difference of the two plates is kept very small by the conducting wire, the copper plate may become sufficiently electronegative to hold its own ions while the zinc plate is still losing ions to the solution. When this condition has been reached, the copper ions of the solution which come into contact with the copper plate are held to its surface, and are replaced in the solution by ions from the zinc plate. Meanwhile, electrons continue to flow through the connecting wire from zinc to copper, and to combine in the copper plate with the new electropositive ions which are being deposited upon its surface from the solution. Since there is a greater cohesion between copper ions and electrons than between zinc ions and electrons, this change results in a decrease of the potential energy of the system and a consequent increase in kinetic energy. The kinetic energy of the voltaic cell is accordingly due to the difference in the cohesion between positive sub-atoms and electrons in the two metals. The voltaic cell is an engine run by cohesion.

We see, then, that in the case of the Daniell's cell no negative ions either enter or leave the solution. Both positive and negative ions un-

doubtedly exist in the solution, and under the impulse of the electric field the positive ions drift in one direction and the negative ions in the opposite direction, yet the current in the solution is, on the whole, due to the drift of the positive ions through the solution from the zinc to the copper.

Evidently, there is nothing in the process as described above to tell us anything about the charges on the zinc and copper ions while in the solution. All that we can know from Faraday's laws is that 96470 coulombs of electrons flow through the metallic part of the circuit while one gram-atom of monovalent metallic ions is dissolved off from one electrode and one gram-atom of another or the same monovalent ion is deposited upon the other electrode. If the ions are bivalent, as in the case of zinc and copper, then twice this quantity of electricity must flow around the metallic circuit while one gram-atom of metallic ions is being transferred through the solution. The electricity which flows through the metallic part of the circuit does not pass through or into the liquid at all.

It is true, as argued by Arrhenius, that in the case of the Daniell cell the copper sulphate solution is changed into a zinc sulphate solution, and unless the positive charges of the zinc and copper ions are equal zinc sulphate should be electropositive or electronegative to copper sulphate. Since both are conductors, in practice both are regularly found to be charged to nearly the same potential as the earth. So far as is known, no one has separated the resulting compounds and tested their charges after a chemical reaction, as assumed by Arrhenius. It is true that the metals, even after being discharged to earth or to the inside of the same hollow conductor, are capable of inducing easily appreciable charges upon each other when they are brought near together.

Ionic Mobility and Ionic Charges

Since the electrolytic process gives us no method of measuring directly the charges upon the metallic ions in electrolysis, we can only infer the magnitude of these charges from other considerations.

One method of doing this, and the one to which special attention is called in this paper, is by their rate of drift through the solution under the impulse of an external electric field.

In 1853, Hittorff found that after a current has been set up in an electrolyte for a short time the homogeneity of the solution has been disturbed, so that the concentration of the solution usually becomes greater about one electrode than about the other. Hittorff attributed this condition to a difference in the velocities of drift of the positive and negative ions, and undertook to determine the velocities of drift of a number of ions.

Hittorff's method was based upon the Grotthuss hypothesis as to the mechanism of dissociation in the cell.² According to this hypothesis the first manifestation of the current consists in bringing the molecules of the substance which is to be dissociated into such orientation that the cation of every molecule is turned toward the cathode and the anion toward the anode. The two ions of each pair then separate and move in opposite directions, the anions toward the anode and the cations toward the cathode. By this means all the ions except the two at the end of the row exchange partners, combining with the oppositely charged ion from the nearest molecule on the side toward which they are moving. The two ions at the end of the row go to their respective electrodes, the anion to the anode and the cation to the cathode.

Hittorff reasoned that if one kind of ion traveled with a greater speed than the other kind, the new molecule would, each time, be formed a little farther along in the direction taken by the faster ion, so that there would be, on the whole, a drift of the dissolved electrolyte in one direction. This would result in an increase of concentration around the electrode toward which the faster ion was traveling, and Hittorff undertook to calculate from the measurement of this concentration the relative velocities of the two ions.

As the result of a long series of investigations, Hittorff arrived at the conclusion that in an electric field of a given strength any given electrolytic ion has the same velocity, regardless of the molecule from which it was derived, and he determined these velocities relative to each other for a considerable number of ions.

The investigations of Hittorff were greatly extended by F. Kohlrausch and his students. Kohlrausch's work was largely based upon the assumption that the current through the solution was due to the combined effect of the positive ions carrying charges in one direction and the negative ions carrying charges of opposite sign in the opposite direction. Then, since he believed that every monovalent ion of either sign carried a charge of the same magnitude, he stated the law that the molecular conductivity of a solution at infinite dilution (that is, a gram-molecule of any substance dissolved in sufficient water so that its molecules will, according to theory, all be dissociated) may be calculated as the sum of two numbers, one of which depends only upon the cation and is independent of the anion, and the other of which depends upon the anion and is independent of the cation. These two numbers he regarded as depending only upon the velocities of the ions, since all ions were regarded as carrying charges of the same magnitude.

It will be seen that from the point of view presented in this paper

² *Poggendorff's Annalen*, 89, 181 (1853).

the conductivity of a solution will be determined largely by the mobility of the cations, since the more rapidly these travel through the solution to the cathode the more rapidly will others leave the anode and the more rapidly will electrons be transferred through the metallic part of the circuit from the anode to the cathode.

Kohlrausch was able to calculate by means of his hypothesis the conductivities of a number of substances in which both ions are monovalent, but his law seemed to break down entirely for other substances. True, the exceptions to the rule could generally be explained on the assumption of more complex ions, or the dissociation into simpler ions than were known to exist in the solution, or on the assumption that the ions gathered about them larger or smaller spheres of the solvent which had to be carried with them; but while these assumptions, which could neither be proved nor disproved, might assist the proposer of a theory to "save his face" they did not increase the usefulness of the theory for calculating molecular conductivities of electrolytes.³

While Kohlrausch's calculations of ionic mobility were based upon inadequate theory, there seems to be no question that different ions are impelled with different speeds in the same electric field. A few ions have had their speeds measured experimentally by methods well known to the physical chemist, and a considerable number of others have had their speeds calculated by the methods of Hittorff, Kohlrausch and others, so that there is now substantial agreement regarding the velocities of a considerable number of ions in very dilute water solutions and under the impulse of a standard electric field.

In Table I are given the calculated mobilities of a number of ions in an electric field of one volt per centimeter as selected by Kaye and Laby for their book of tables. The mobilities have been multiplied by one-hundred-thousand to reduce them to whole numbers, and accordingly represent the ionic velocities in hundred-thousandths of a centimeter per second.

TABLE I.
Mobility of Ions.

| | | | | | | | |
|----|------|-----------------|------|-----|------|------------------|------|
| H | 330 | NH ₄ | 66.3 | ½Zn | 48.4 | F | 48.3 |
| Li | 34.6 | Tl | 68.4 | ½Cu | 49 | Cl | 67.8 |
| Na | 45.2 | ½Ca | 53.7 | Ag | 56 | Br | 70 |
| K | 67 | ½Sr | 53.6 | ½Cd | 49.2 | I | 68.8 |
| Rb | 70.5 | ½Ba | 57.5 | ½Pb | 63.5 | NO ₃ | 64 |
| Cs | 70.5 | ½Mg | 47.7 | OH | 180 | ½SO ₄ | 71 |

The actual values for the bivalent ions are half the above numbers, but since in the theory just considered each bivalent ion is assumed to

³ In this connection, see Arrhenius: "Electrochemistry," pp. 143-44.

carry twice the charge of a monovalent ion their speeds are multiplied by two to make them fit into the equations which actually apply only to monovalent ions.

The following ions have had their speeds measured experimentally: K, 55.3; Na, 31.8; Ba, 33; Mg, 16.7; Cl, 52.9; SO_4 , 30.4.

It is plain from the comparison of the calculated and measured velocities of the same ion that in the case of ionic mobilities the results of theory and experiment are still very far apart. The difficulties in the direct measurement of ionic mobilities are considerable and the experimental errors in measuring such small variations from the normal speeds of diffusion of the ions are undoubtedly proportionally very great. As a consequence of these difficulties, physical chemists have come to look upon the calculated values as the more trustworthy of the two. The best we can do in the present state of our science is to treat them as giving approximately correct *relative* values of ionic mobilities, and it seems probable that in the case of the monovalent elements these approximations are not very far from the true values.

Assuming that we know with a fair degree of approximation the relative mobilities of the ions of a single group of similar elements, we may infer with a similar degree of probability the corresponding ionic charges.

If, as was assumed by Faraday, the monovalent ions all have charges of equal magnitude, they must be driven by equal electrical forces and the differences in their speeds must be due to a difference in the resistance with which they meet in moving through the water. According to this point of view, this resistance is a true frictional resistance, and it turns out to be very great.

Thus the force which must act upon one gram-ion of hydrogen when completely dissociated in water to give it a velocity of one centimeter per second amounts to 302,000,000 times the weight of a kilogram, and on a gram-ion of lithium it is nearly ten times as great, amounting to approximately one ten-thousandth dyne for each ion.

Since these ionic speeds are taken for very dilute solutions, the difference in viscosity of the different solutions must be very small. The greater retardation of some ions than of others is accordingly not due to the greater viscosity of the solution in which they are contained. The viscosity of a normal hydrochloric acid solution is more than nine per cent greater than that of a potassic chloride solution of the same concentration, yet in a given electrical field the hydrogen ions in the hydrochloric acid solution move with five times the speed of the potassium ions in the potassic chloride solution. If the potassium ions meet with five times as great resistance to their motion through water as do the hydrogen ions,

it would seem that this, of itself, should make the viscosity of a solution of potassium ions greater than that of a similar solution of hydrogen ions, whereas the addition of hydrogen ions to water seems to make the viscosity greater, while the addition of potassium ions certainly diminishes it.

Again, if the resistance is due to friction between the moving ions and water, it would seem that the larger ions should meet with the greater resistance. This seems not to be the case. The volumes of metallic ions are generally assumed to be proportional to the volumes of their gram-atoms in the solid state. Heydweiller has calculated the volume of a gram-atom of various elements when existing in the form of ions in water solution on the assumption that the volume of the water, itself, remains unchanged by the solution of the ions. While this assumption is certainly not justified, yet the two methods give the same order of magnitudes, and in both cases the larger ions have the higher speeds in electrolysis. In Table II, the relative ionic volumes as estimated by the two methods and the ionic speeds of the alkali metals are given.

TABLE II.

Ionic Volumes and Ionic Speeds of Alkali Metals.

| Element | Vol. of Gram-atom | Heydweiller's Vol. | Ionic Speed |
|---------|-------------------|--------------------|-------------|
| Li | 12.9 | 2.8 | 34.6 |
| Na | 23.7 | 3.6 | 45.2 |
| K | 45.4 | 7 | 67 |
| Rb | 56.1 | 9.3 | 70.5 |
| Cs | 70.6 | 12.8 | 70.5 |

It will be seen from the above table that until the atomic volume becomes large the mobilities of the ions increase approximately proportionally to their increase of volume. Since the larger and heavier ions move with the higher speeds, it would seem that they must be acted upon by greater forces. Since in a field of unit strength the forces acting upon the ions are equal to their electrical charges, it seems impossible to avoid the conclusion that the larger ions have greater electrical charges than the smaller ions.

Another assumption which is involved in the Kohlrausch theory is that the dissociated ions remain free for considerable periods of time, so that the speeds measured in electrolysis are the maximum speeds which the ions may attain under the acceleration of the electric field. This is plainly contrary to the views of Faraday, who says in paragraph 524 of "Experimental Researches":

I do not believe that a substance can be transferred in the electric current beyond a point where it ceases to find particles with which it can combine. This was also the assumption of the original Grotthuss hypothesis.

Computation of Ionic Charges

If, as was believed by Faraday, the ions are free for only very short periods, their motion will be accelerated throughout the whole period of freedom. If different ions are free for the same periods of time in solutions of the same concentration, their measured speeds will be proportional to their accelerations by the electric field. Under these conditions, the forces acting upon the ions must be proportional to the products of their speeds into their ionic masses, that is, the ordinary mechanical equation for acceleration, $F = ma$, must apply to the ions.

In this equation, F = the electric force acting upon the ion, and is the product of the field strength into the ionic charge, Q . In an electric field of unit strength, $F = Q = ma$, where m = the mass and a the acceleration of the ion. If the ionic mobility may be substituted for the ionic acceleration, the charge of an ion becomes equal to the product of its ionic mass into the number representing its ionic mobility.

In Table III the relative values of Q are computed for three of the best known groups of elements, using the ionic mobilities as given in Kaye and Laby's tables. The data for computing these values for any other complete group are not known. The charge of hydrogen is also computed so that, if desired, the other charges may be taken in terms of the hydrogen charge.

TABLE III.
Relative Ionic Charges.

| Element | Ionic Speed | Atomic Weight | Ionic Charge | Charge H = 5 |
|---------|-------------|---------------|--------------|--------------|
| H | 330 | 1 | 330 | 5 |
| Li | 34.6 | 7 | 242.2 | 3.6 |
| Na | 45.2 | 23 | 1038 | 15.7 |
| K | 67 | 39 | 2611 | 39.6 |
| Rb | 70.5 | 85.5 | 6030 | 91.2 |
| Cs | 70.5 | 132.8 | 9350 | 142 |
| F | 48.3 | 19 | 918 | 14.6 |
| Cl | 67.8 | 35.5 | 2410 | 36.5 |
| Br | 70 | 80 | 5600 | 84.9 |
| I | 68.8 | 127 | 8750 | 132.5 |
| Mg | 47.7 | 24.3 | 1156 | 17.4 |
| Ca | 53.7 | 40 | 2151 | 32.5 |
| Sr | 53.6 | 87.6 | 4700 | 71.5 |
| Ba | 57.5 | 137.4 | 7900 | 119.4 |

When the above numbers in the different groups are compared, it will be seen that there is a similar regularity in each group, so that for any atom in a given group a corresponding atom may be found in another group, and that the ratios of the charges of the two corresponding atoms of a pair is nearly a constant for any two groups. Thus for the alkali metals and the halogen group, $\text{Na:F} = 1.13$, $\text{K:Cl} = 1.08$, $\text{Rb:Br} = 1.08$, $\text{Cs:I} = 1.07$.

Ionic Charges and Cohesion

That a relation between ionic charges and cohesion should be suspected may be seen from the following considerations: We have seen that Bennett and Cavallo inferred from the contact charges of metals that some metals have a greater "affinity" or "adhesive power" for the electric fluid (electrons) than do others. Accordingly, when two metals are brought into contact the one which has the stronger affinity for the electric fluid will take some of this fluid from the other and leave it with a deficiency. We now know that a metal which has an excess of the electric fluid is negatively electrified and one which has a deficiency is positively electrified, consequently the metal which becomes negatively electrified is the one which has the greater affinity for electrons.

Again, if cohesion and chemical affinity are merely electric attractions between positively and negatively charged atoms or parts of atoms (ions), as was believed by Davy, Berzelius and Faraday, these forces must, in their final resolution, consist in the mutual attractions of two or more positively charged ions for the same electron or electrons. These electrons may be permanently attached to one of the atoms, or they may be capable of being separated from both, but the final result will be the same. In both cases it will follow that the metals whose ions hold the electrons with the weakest forces, and which are consequently most electropositive in the contact series, will have the weakest cohesion.

It was shown by the present writer in 1908⁴ that there is a definite relation between the contact electrical series and the properties which depend upon cohesion. Since cohesion cannot be measured directly, it is necessary to estimate its magnitude by means of some measurable quantity which is known to depend upon it. A number of such quantities are known, and in the paper referred to above the compressibilities, melting points, expansion coefficients and hardness were used. It was assumed that the greater the cohesion, the lower the compressibility and expansion coefficients and the higher the melting point and the greater the hardness of the metal. The table showing the relation of these properties to the position of the element in the contact electric series is reproduced in Table IV.

⁴ *Physical Review*, 26, 410 (1908).

TABLE IV.
Relation of the Contact Electromotive Series to Cohesion.

| Voltaic Series | Compress- ibility | Melting Point | Expansion Coefficient | Hardness |
|----------------|----------------------|------------------|--------------------------|----------|
| Caesium | 61 | 26.5 | .00029 | .2 |
| Rubidium | 40 | 38.5 | .00027 | .3 |
| Potassium | 31.5 | 58 | .00025 | .5 |
| Sodium | 15.5 | 95 | .00021 | .4 |
| Lithium | 8.8 | 180 | .000072 | .6 |
| Zinc | 1.5 | 419 | .000029 | 2.5 |
| Lead | 2.2 | 330 | .000028 | 1.5 |
| Tin | 1.67 | 230 | .000022 | 1.8 |
| <i>Iron</i> | .38 | 1500 | .000012 | 4.5 |
| Silver | .82 | 950 | .000019 | 2.5—3. |
| Copper | .54 | 1054 | .000017 | 2.5—3. |
| Gold | .47 | 1035 | .000015 | 2.5—3. |
| Platinum | .21 | 1780 | .000009 | 4.3 |
| Carbon | .5 | Unmelted | .000005 | 10. |

The one metal which seems from the above table to be conspicuously out of place in the contact series is iron. This exception may be only apparent. The properties given in the above table would seem to place iron just above platinum in the contact series. There are many reasons for thinking that it actually belongs there.

It is well known that iron may exist in two states, known as the active and passive states. In the active state iron oxidizes readily and is very readily attacked by dilute acids. It is in this state that it occupies the position in the voltaic series which is usually assigned to it. In the passive state it seems to come in its proper position in the contact series.

It has generally been believed that the active state of iron is the normal state, and that passivity is an induced condition. In recent years this opinion has changed, and there is now much experimental work to show that the passive state is the normal state.⁵ The above table would seem to contribute to this point of view. Recent experiments made by the writer have shown that an iron rod when made passive by fuming with nitrous oxide gas becomes thereby strongly electronegative, and other experiments made in the Stanford laboratory have shown that the ferric ion is strongly electronegative in the metallic series.

Zinc also seems out of place in the series as indicated by all its properties considered except its expansion coefficient. Zinc and lead are sometimes transposed in the series, and are always very near together,

⁵ See Grave, *Zeitschrift für physikalische Chemie*, **77**, 513 (1911). Adler, *ibid.*, **80**, 385 (1912). *Transactions of the Faraday Society*, **60**, pt. 3, March, 1914.

but the above data would seem to place zinc between tin and silver, which seems less probable than that it is between lead and tin.

Since the above table was published, I. Traube⁶ has calculated by means of the Van der Waals formula the internal pressure, $a/v\%$, due to cohesion of a number of metals. His calculations put them in the order of increasing pressure as follows:

| Metal | $a/v\%$ | Metal | $a/v\%$ |
|-----------|---------|----------|---------|
| Potassium | 8190 | Silver | 161900 |
| Sodium | 18500 | Gold | 178500 |
| Lead | 51500 | Copper | 236100 |
| Tin | 68700 | Iron | 323900 |
| Zinc | 108900 | Platinum | 324200 |

Traube says:

If one calculates with the help of Van der Waals' equation the quantity $a/v\%$, which may be regarded as an approximate measure of the surface tension, the electric potential difference of the metals, and accordingly the Volta series, runs parallel to this surface tension series in the most surprising manner.

Returning now to a consideration of the charges of ions in electrolysis, we have seen reasons for expecting a relation between these charges and the cohesion of the element from which they are derived, and for expecting that the ions having the highest positive charges in a given group will come from the element of the group in which cohesion is weakest. Accordingly, cohesion should decrease with an increase of the positive charge of the ions of a given group, and should increase with an increase of the negative charge.

In estimating cohesion we are compelled, as before, to depend upon the magnitudes of certain measurable quantities which must vary with cohesion. Since for similar elements it is reasonable to assume that cohesion varies inversely as the compressibility, we should expect the compressibility to increase as the positive charge of the ion increases.

Fortunately, we have two groups of ions for which the compressibility is known and for which the ionic charges may be computed. One of these groups consists of positive and the other of negative ions. If our assumption is correct, the compressibility should increase as the positive charge of the ions increases and should decrease as the negative charge increases. That this is true for the positive ions of the alkali metals and the negative ions of the halogen group may be seen from Table V, in which the compressibilities are taken from Richards's determinations.⁷

⁶ *Deutsche physikalische Gesellschaft. Berichte*, 1909, p. 231.

⁷ *Zeitschrift für physikalische Chemie*, **61**, 1907, and *Journal of American Chemical Society*, 1911. See, also, Kaye and Laby's Tables.

TABLE V.
Ionic Charges and Compressibility.

| Element | Comp. $\times 10^6$ | Ionic Chg. | Element | Comp. $\times 10^6$ | Ionic Chg. |
|---------|---------------------|------------|---------|---------------------|------------|
| Li | 8.8 | + 3.6 | Cl | 95 | — 36.5 |
| Na | 15.4 | + 15.7 | Br | 51.8 | — 84.9 |
| K | 31.5 | + 39.6 | I | 13 | —132.5 |
| Rb | 40 | + 91.2 | | | |
| Cs | 61 | +142. | | | |

The relation between compressibility and ionic charge is shown graphically in Figure 1.

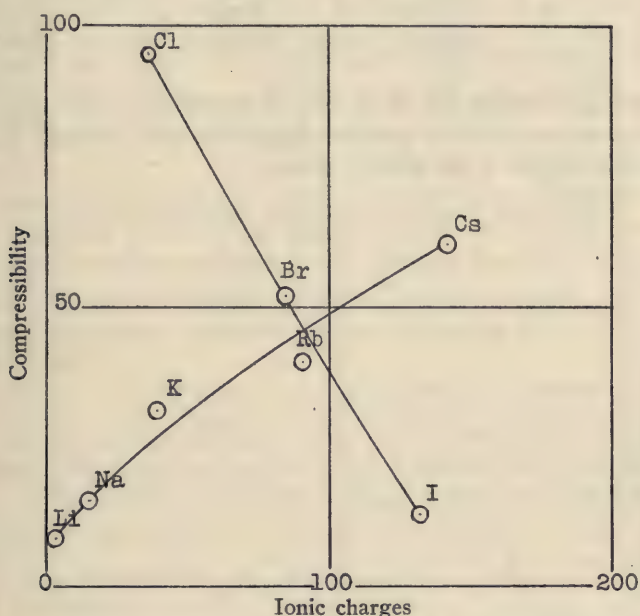


FIGURE 1. Relation of Compressibility to Ionic Charge.

In Table IV the expansion coefficients are also used as a measure of cohesion. It is plain that for a given increase of atomic kinetic energy the expansion should be greater the weaker the cohesion between the atoms. Accordingly, when the elements of a given group are arranged in the order of their expansion coefficients they should be arranged in the inverse order of their cohesion constants.

Unfortunately for our purpose, there is no complete group of similar elements whose expansion coefficients are known and the mobilities of whose ions in electrolysis are also known. In "Science Abstracts," A, 17,

No. 2015, is a reference to an article on the properties of the alkali metals in which the expansion coefficients in both the solid and liquid states are given for four of these metals. These expansion coefficients are given in Table Va, and in Figure 2 their mean values are plotted against the ionic charges.

TABLE Va.
Expansion Coefficients and Ionic Charges.

| Element | Expansion Coefficient | | |
|---------|-----------------------|---------|---------|
| | Solid | Liquid | Mean |
| Na | .000216 | .000274 | .000245 |
| K | .000250 | .000283 | .000266 |
| Rb | .000270 | .000338 | .000304 |
| Cs | .000290 | .000345 | .000317 |

A glance at the table will show that, in accordance with expectation, the expansion increases as the positive charge increases, though the figure shows that the relation is not strictly linear.

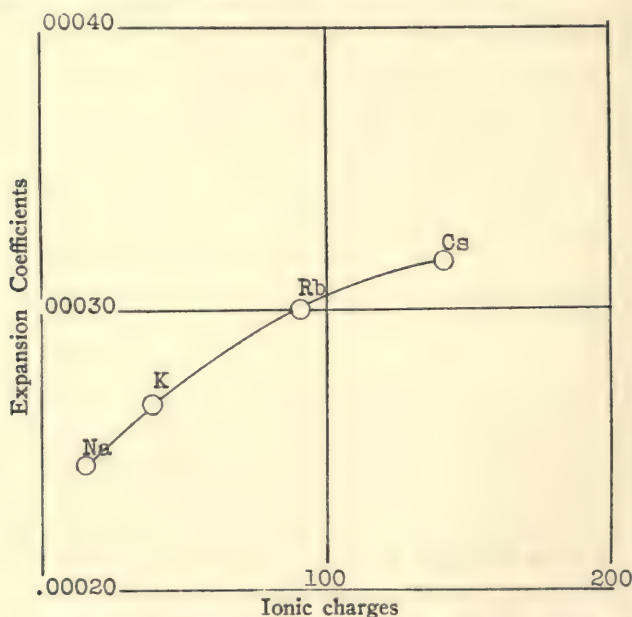


FIGURE 2. Relation Between Expansion Coefficients and Ionic Charges.

The melting point was also referred to as one of the constants which may be used in estimating cohesion. Since solids liquefy when the kinetic energy of their atoms becomes so great that cohesion can no longer hold

them in permanent positions, and since the atoms of all solids are supposed to have the same kinetic energy at the same temperature, the melting point of a solid must be higher the greater the cohesion between its atoms. If cohesion decreases as the positive charge of the atoms increases, then the higher the positive charge of the ions of an element the lower should be its melting point. That this relation holds for both the positive alkali metals and the negative halogen elements may be seen from Table VI. The melting points are given in absolute temperature.

TABLE VI.
Melting Points and Ionic Charges.

| Element | Melting Pt. | Ionic Chg. | Element | Melting Pt. | Ionic Chg. |
|---------|-------------|------------|---------|-------------|------------|
| Li | 459 | + 3.6 | F | 50 | — 14.6 |
| Na | 370 | + 15.7 | Cl | 171 | — 36.5 |
| K | 335 | + 39.6 | Br | 266 | — 84.9 |
| Rb | 311 | + 91.2 | I | 386 | —132.5 |
| Cs | 299 | +142. | | | |

The fourth property which was used as an index of cohesion was hardness, and we see from Table IV that the hardness increases from Caesium to Lithium while the ionic charges increase in the inverse order. In the case of the halogen elements Iodine is a solid, Bromine a liquid, Chlorine an easily liquefiable gas and Fluorine a gas which is liquefied with difficulty.

COHESION BETWEEN IONS AND WATER

While the data already given seem to indicate beyond a doubt that the ionic charge is a prominent factor in determining the cohesion between atoms of the same kind, they do not show that cohesion between atoms of different kinds is determined in the same manner. It may be shown, however, that the cohesion of ions for water in which they are dissolved is also determined by their electric charges.

One of the most direct methods of measuring cohesion between a dissolved substance and its solvent is by means of volume changes in the solvent. This method has been used with considerable success by A. Heydweiller in a series of investigations, the results of which he has published in *Annalen der Physik*. In these papers Heydweiller has given for a large number of chemical elements a cohesion constant by means of which he is able to calculate the cohesion between water and various compounds of these elements. This constant he calls the *Ionenmodulus*. It indicates the percentage increase of the density of the water in which the ions are dissolved, assuming that the density of the dissolved substance is unchanged by solution. The values are extrapolated for infinite dilution from curves plotted for various concentrations.

The values of this constant, A_s , are to be found in Tabelle 30¹ *Annalen der Physik*, 37, 765. These values may be calculated approximately by multiplying the ionic charges by a constant which is different for monovalent and bivalent elements. Since the ionic charges are calculated from the products of the mass and mobility of the ion, we may write $A_s = mvk$, where m is the mass and v the mobility of the ion and where $k = 0.00112$ for univalent ions and $k' = 0.00372$ for divalent ions. This relation is shown in Table VII for all the ions whose mobility is known and for which Heydweiller has calculated his *Ionenmodulus*. The mobilities are taken from Kaye and Laby's Tables. The velocities are those actually observed, i.e., one half the values usually taken in the case of divalent ions. If the usual values of the divalent ions be used, k' becomes 0.00186.

TABLE VII.

Relation of Heydweiller's Ionenmodulus to Ionic Charges.

| Ion | Mobility | Mass | mvk | A_s |
|--|----------|----------------|-------|-------|
| | | $k = 0.00112$ | | |
| Li | 34.6 | 7 | .27 | .35 |
| Na | 45.2 | 23 | 1.31 | 1.38 |
| K | 67 | 39.1 | 2.34 | 2.10 |
| Rb | 70.5 | 85.45 | 6.9 | 6.32 |
| Cs | 70.5 | 132.81 | 10.50 | 10.58 |
| NH ₄ | 66.3 | 18 | 1.33 | .98 |
| Cl | 67.8 | 35.46 | 2.70 | 3.02 |
| Br | 70 | 79.92 | 6.28 | 6.68 |
| I | 68.8 | 126.92 | 9.80 | 10.27 |
| OH | 180 | 17 | 3.46 | 3.40 |
| NO ₃ | 64 | 62 | 4.68 | 4.54 |
| C ₂ H ₃ O ₂ | 42.1 | 59 | 2.78 | 3.04 |
| | | $k' = 0.00372$ | | |
| H | 330 | 1 | 1.22 | 1.05 |
| F | 48.3 | 19 | 3.42 | 3.16 |
| Mg | 23.8 | 24.32 | 2.17 | 2.66 |
| Ca | 26.8 | 40.09 | 4.00 | 4.04 |
| Sr | 26.8 | 87.62 | 8.74 | 8.76 |
| Ba | 28.7 | 137.37 | 14.66 | 13.08 |
| Cd | 24.6 | 112.40 | 10.30 | 10.86 |
| Pb | 31.7 | 207.1 | 24.4 | 20.68 |
| Cu | 24.5 | 63.57 | 5.79 | 7.26 |
| Zn | 24.2 | 65.37 | 5.88 | 7.22 |
| Ag | 56 | 107.88 | 22.46 | 10.02 |
| SO ₄ | 35.5 | 96 | 12.65 | 11.54 |

It will be seen that the values of A_s calculated above differ from Heydweiller's values by less than the probable error of determination except in a few cases. Hydrogen and fluorine are placed with the divalent elements, though they belong in the monovalent group, and copper and

zinc give too low values of A_s . Silver is placed in the divalent group, where its value is twice as great as given by Heydweiller. If placed in the monovalent group, its value, like the values of zinc and copper, is too low. Notwithstanding these discrepancies, the evidence seems conclusive that the quantity which we have called the ionic charge is an important determining factor in the cohesion between these ions and water. It will be observed that in this case, since the attraction is between the electric charge of an ion and the induced charges of the nearly neutral water molecules which surround it, the attraction increases with the charge of the ion, whether that charge be positive or negative. The reason why this is not the case within a metal will be discussed under the head of Ionic Charges and Specific Inductive Capacity.

COHESION OF COMPOUND MOLECULES

If we conceive of the atoms of a solid as being held together by their electric attractions, either for one another or for electrons, the attractions between compound molecules must be of the same nature. We have no way of computing the charge of a compound molecule unless we assume that when positive and negative ions combine the resultant charge is the algebraic sum of the ionic charges before combining. This may, or may not, be the case, since it is possible that electrons may be taken up or set free in the chemical reaction by which the compound is formed. In the case of the halides of the alkali metals it seems probable that the ions which are set free in water solution are the only ones in the molecules. By assuming the molecular charge to be the sum of these ionic charges we may accordingly calculate the molecular charges of these salts.

The melting points of these salts are known, and we may accordingly compare these melting points with the corresponding molecular charges as we have compared them with the ionic charges of the elementary substances. This is done in Table VIII for the chlorides of sodium, potassium, rubidium and caesium. The molecular charges are taken as the algebraic sum of the charges of their respective ions.

TABLE VIII.
Molecular Charges and Melting Points.

| Salt | Melting Point | Molecular Charge |
|------|---------------|------------------|
| NaCl | 801 | — 20.8 |
| KCl | 770 | + 3.1 |
| RbCl | 710 | + 54.7 |
| CsCl | 631 | +105.5 |

It is seen that here, as in the case of the elementary atoms, cohesion decreases as the positive charge increases. This relation is shown graphically in Figure 3.

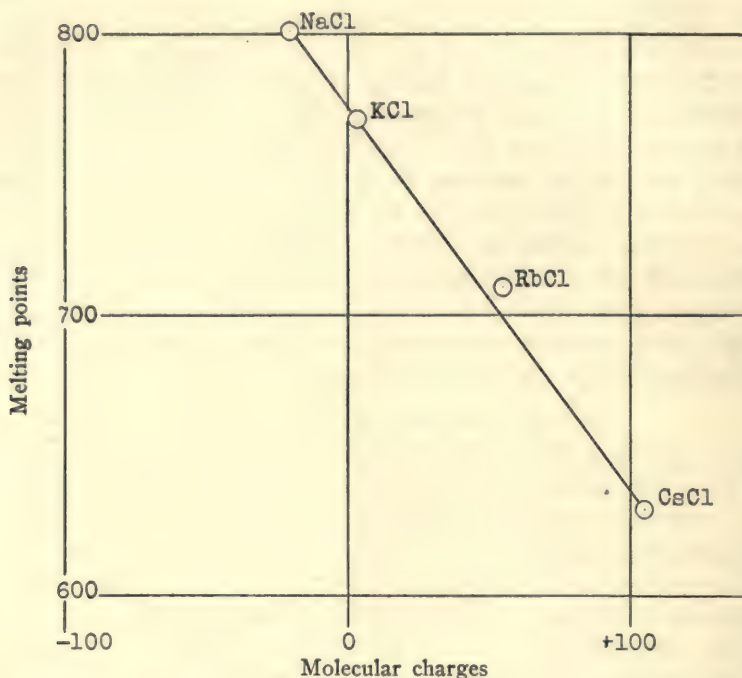


FIGURE 3. Relation between Melting Points and Molecular Charges.

IONIC CHARGES AND BOILING POINTS

It is plain that the boiling point, as well as the melting point, may be used as a measure of cohesion, since it is the temperature at which the kinetic energy of the molecules enables them to escape from cohesion against a definite external pressure. It is plain that the greater the cohesion the higher should be the boiling point, hence the more electro-positive the atoms of an element in a group of similar elements the lower should be its boiling point.

That this is true for the halogen elements may be seen from Table IX, in which the boiling points, absolute, and the negative ionic charges of the elements are given.

TABLE IX.

Ionic Charges and Boiling Points.

| Element | Boiling Point | Ionic Charge |
|---------|---------------|--------------|
| F | 86 | — 14.6 |
| Cl | 239.8 | — 36.5 |
| Br | 336 | — 84.9 |
| I | 457.4 | —132.5 |

The determination of the boiling points of the alkali metals is beset with considerable difficulty, and the results of different determinations differ widely for the same metal. Kroenen has accordingly attacked the problem in another way.⁸ He has measured the vapor pressure of the alkali metals in an atmosphere of pure nitrogen up to a pressure of ten millimeters of mercury, and has determined the temperature corresponding to a given pressure. Since, from the rule of Ramsay and Young, the ratios of the absolute temperatures of the various metals for any given vapor pressure are the same for any other given vapor pressure, the temperatures at any chosen vapor pressure may be taken as a measure of cohesion, just as the boiling points may. The boiling points are the corresponding temperatures for a pressure of 760 millimeters of mercury.

The temperatures at which the various alkali metals have a vapor pressure of two millimeters of mercury are taken from the curves on page 448 of Kroenen's paper, and are as follows: Cs, 304°; Rb, 320°; K, 365°; Na, 420°; Li, 515°. In Figure 4 these temperatures are plotted against the ionic charges of these metals.

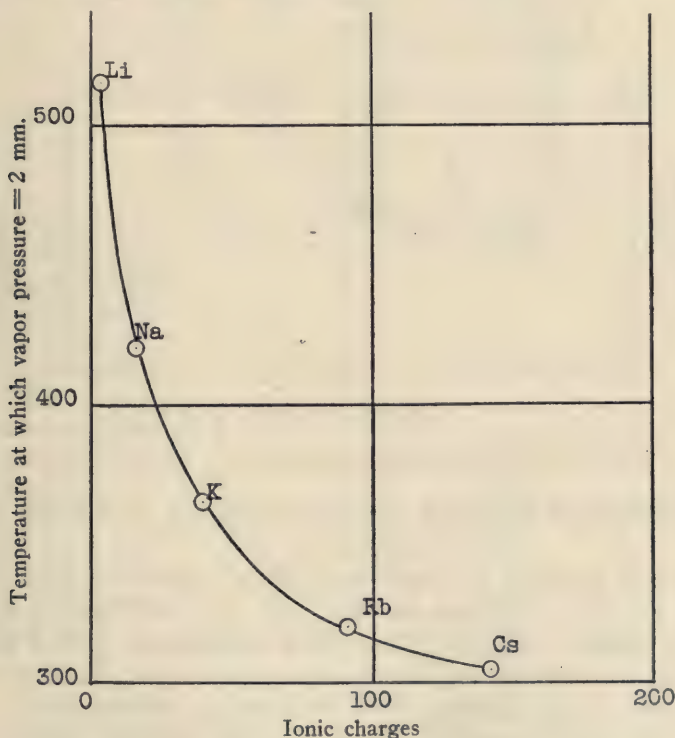


FIGURE 4. Relation of Vapor Pressure to Ionic Charges.

⁸ *Annalen der Physik*, **40**, 438 (1913).

MOLECULAR CHARGES AND BOILING POINTS

It is much more difficult to find data on the boiling points of compounds whose molecular charges we can compute than on their melting points. The boiling points of the hydrogen acids of the halogen group are known. Of these, hydrofluoric acid is regarded by the chemists as an associated liquid and hence as having an abnormal boiling point. The boiling points of the other acids of this group are related to their resultant molecular charges much as are the boiling points of the elements to their ionic charges. The boiling points and resultant molecular charges of these acids are given in Table X. Their relation is shown graphically in Figure 5.

TABLE X.
Molecular Charges and Boiling Points.

| Compound | Boiling Point | Molecular Charge |
|----------|---------------|------------------|
| HI | 239 | -124.5 |
| HBr | 200 | - 78.9 |
| HCl | 193 | - 31.5 |
| HF | 292 | - 8.6 |

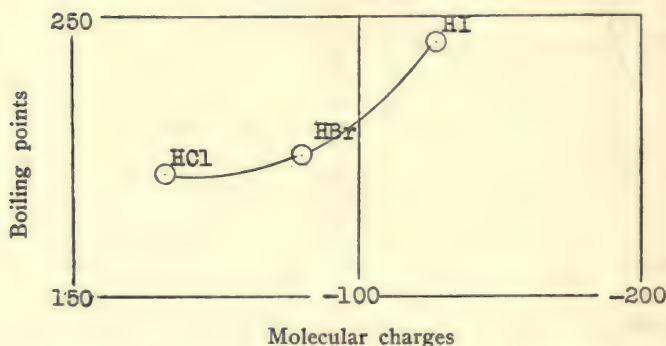


FIGURE 5. Relation of Molecular Charges to Boiling Points.

VAPOR PRESSURE OF AMMONIA OF CRYSTALLIZATION AS RELATED TO THE
NEGATIVE ION OF THE MOLECULE

The part played by the negative charge of an ion in a molecule in its cohesion for other molecules may be shown in a still different way. In an article entitled "Ueber die Natur der Nebenvalenzen,"⁹ Fritz Ephraim has given a large number of determinations of the vapor tension at various temperatures of the ammonia over the hexammoniacates of the haloid salts of the bivalent metals. These salts, the chlorides, bromides and

⁹ *Zeitschrift für physikalische Chemie*, 81, 513.

iodides of many of the bivalent metals, crystallize with ammonia, forming salts with six molecules of ammonia of crystallization.

This ammonia of crystallization may be driven off by heat. Ephraim has measured the ammonia tension over a considerable number of these ammoniacated salts for a considerable range of temperature. He has then calculated for ten or twelve different temperatures the absolute temperature at which each pair of salts would give the same vapor pressure of ammonia, and has expressed this as the ratio of two absolute temperatures. Thus

$$\frac{T \text{ CdBr}_2, 6\text{NH}_3}{T \text{ CdCl}_2, 6\text{NH}_3}$$

gives the ratio of the absolute temperatures at which both salts have the same ammonia pressure over their surfaces. These ratios are constant for a given pair of salts. Some of these ratios are given in Table XI.

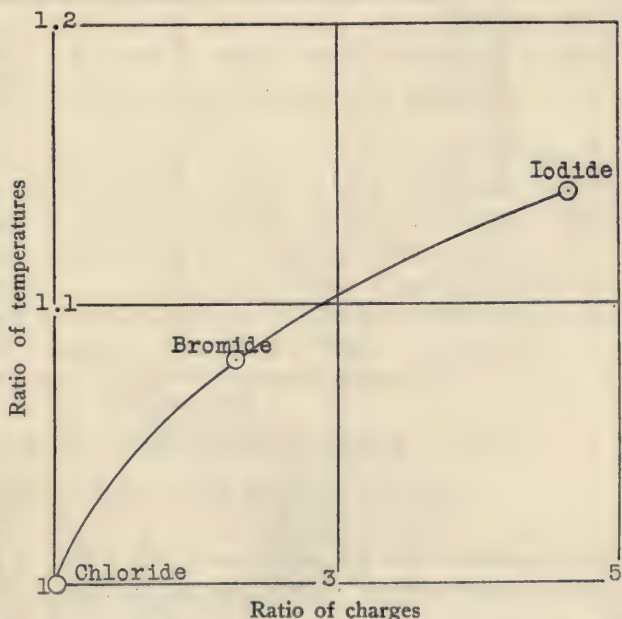
TABLE XI.

| Metal of Salt | Bromides | Iodides |
|------------------|-----------|-----------|
| | Chlorides | Chlorides |
| Cd | 1.074 | 1.145 |
| Zn | 1.026 | 1.014 |
| Mn | 1.112 | 1.232 |
| Ni | 1.072 | 1.131 |
| Co | 1.088 | 1.145 |
| Fe | 1.092 | 1.177 |
| Mean | 1.077 | 1.141 |

Since the ammonia ion is electropositive, it must be held to these salts by the charges of their negative ions. The ratios of the charges of these ions are $\text{Br}/\text{Cl} = 2.32$ and $\text{I}/\text{Cl} = 3.63$. The relation between these two sets of ratios is shown graphically in Figure 6.

FIGURE 6

Ratio of temperatures of equal ammonia tension compared with the ratio of the charges of the negative ion. The abscissas show the ratios of the charge of the negative ion to the chlorine charge. The ordinates show the ratios of temperatures for the same ammonia tension.



CRITICAL TEMPERATURES AND IONIC CHARGES

The critical temperature should serve better as a means of measuring cohesion than any of the other fixed temperatures, since it is the temperature at which the kinetic energy is in equilibrium with cohesion; and critical temperatures have been used in calculating cohesion constants by various methods. Unfortunately, the critical temperatures are known for only a few elements, and these are principally elements whose ionic mobilities in water solutions are not known.

The critical temperatures of three of the halogen elements, chlorine, bromine and iodine, have been determined. The values found by different investigators differ by seven degrees for chlorine and ten degrees for iodine, while bromine has been determined but once. Taking the mean of the values given, the critical temperatures, absolute, of these three elements are as follows: chlorine, 418; bromine, 575; iodine, 780. These numbers are plotted against the ionic charges of these three elements in Figure 7, and it is seen that one set of quantities may be calculated from the other within the limits of uncertainty of either.

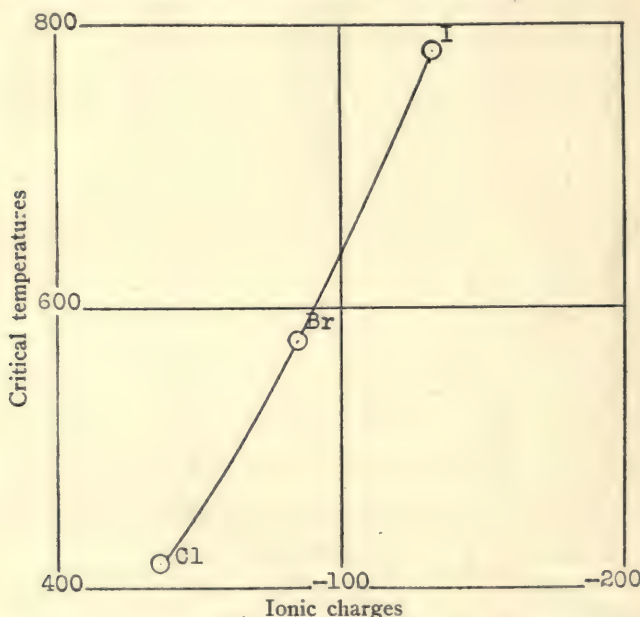


FIGURE 7. Relation of Critical Temperatures to Ionic Charges.

MOLECULAR CHARGES AND CRITICAL TEMPERATURES

It has already been shown that when the three elements given above were combined with hydrogen the boiling points of the compounds were plainly related to their resulting molecular charges. This relation is still

more apparent for the critical temperatures of these acids. These critical temperatures are given in Landolt and Boernstein's Tables, and are shown with their corresponding molecular charges in Table XII.

TABLE XII.
Molecular Charges and Critical Temperatures.

| Acid | T_c | Mol. Chg. |
|------|-------|-----------|
| HCl | 325 | — 31.5 |
| HBr | 364 | — 80. |
| HI | 424 | —127.5 |

By plotting the above quantities against each other, it will be seen that while the critical temperatures of all the halogen ions have been lowered by the combination with hydrogen, the relations to the molecular charges are as close as to the ionic charges.

ATOMIC HEAT OF FUSION AND IONIC CHARGE

The latent heat of fusion of an element may be taken as a measure of its cohesion at the melting point, since it is an expression for the potential energy which the atoms acquire in passing from the solid to the liquid state. Accordingly, if cohesion is greater in electronegative than in electropositive elements, we should expect them to show a higher heat of fusion than the electropositive elements.

Since we have already seen that the melting points of electronegative elements are higher than those of the more electropositive elements of the same group, we know that the latent heat of fusion cannot give the whole measure of the difference in cohesion between them at ordinary temperatures. It does, however, give an indication of this difference at corresponding temperatures.

Landolt and Boernstein's Tables give the atomic heat of fusion of four of the elements whose atomic charges we have calculated. Two of these are alkali metals and two are electronegative elements of the halogen group. They are potassium, sodium, bromine and iodine. In Table XIII are given their ionic charges and their atomic heats of fusion, while in the fourth column are given the atomic heats of fusion calculated from the ionic charges by the empirical formula $L_a = (150 - Q) 0.0053$, where L_a = atomic heat of fusion and Q = the ionic charge.

TABLE XIII.
Atomic Heat of Fusion and Ionic Charge.

| Element | Q | L_a obs. | L_a calc. |
|---------|--------|------------|-------------|
| K | + 39.6 | .60 | .58 |
| Na | + 15.7 | .70 | .71 |
| Br | — 84.9 | 1.3 | 1.25 |
| I | —132.5 | 1.5 | 1.5 |

It will be seen from Table XIII that notwithstanding that the elements given are from the two groups most widely separated in their electrical and chemical properties, their latent heats of fusion may be calculated from their ionic charges as closely as they can be experimentally determined.

IONIC CHARGES AND SURFACE TENSION

One property of liquids which we know is directly due to cohesion is surface tension. Unfortunately, we cannot measure the surface tension of any group of elements whose atomic charges we can calculate. Indirectly, however, R. D. Kleeman¹⁰ has computed for a number of elements a cohesion constant, C_a , which seems to determine the part played by their atoms in the surface tension of the liquid of whose molecules they form a part. This constant, he concludes, depends only upon the nature of the atom, regardless of the other atoms with which it is combined.

In Table XIV are given the values of C_a as calculated by Kleeman, and in the third column are given these values for the halogen elements calculated from the empirical formula $C_a = Q/12 + 4.5$, where Q = the ionic charge. It will be seen that these calculated values agree within the probable error of Kleeman's determination with the values which he adopts.

TABLE XIV.
Kleeman's Cohesion Constant and Ionic Charges.

| Element | C_a | C_a calc. | Element | C_a | C_a calc. |
|---------|-------|-------------|---------|-------|-------------|
| H | 1 | 1 | Cl | 8.40 | 7.50 |
| C | 5.30 | | Br | 10.65 | 11.35 |
| O | 5.94 | | I | 15.49 | 15.20 |
| F | 5.76 | 5.62 | Sn | 14.68 | |

INFLUENCE OF THE IONIC CHARGES OF THE ALKALI METALS UPON THE SURFACE TENSION OF MERCURY IN WHICH THE METALS ARE DISSOLVED

We have seen that the surface tension of a liquid decreases as its ions become more electropositive. Accordingly, if an electropositive metal be dissolved in a less electropositive liquid metal, it should lower its surface tension in proportion to the excess of the positive charges of its ions over those of the metal solvent.

In a paper by Friederich Schmidt, entitled "*Die Veraenderung der Oberflaechenspannung des Quecksilbers durch Metallzusatz*,"¹¹ are given the changes in surface tension of mercury due to the solution of given

¹⁰ *Philosophical Magazine*, 19, 784 (1910).

¹¹ *Annalen der Physik*, 39, 1108 (1912).

percentages of other metals. When the maximum change due to the solution of a given metal is plotted against the ionic charge of that metal a close relation is seen. The relation is still more striking when the lowering of surface tension due to a given concentration is compared with the ionic charges of the dissolved metals.

Metals which lie very near to mercury in the contact electromotive series cause very little change in the surface tension. The alkali metals produce a very considerable change. The more electropositive the metal, the more it lowers the surface tension, and in the case of the alkali metals this lowering is strictly proportional to the ionic charge of the dissolved metal.

From the curve on page 1128 of Schmidt's paper the lowering of surface tension for one atom of the dissolved metal in 5,000 atoms of mercury may be calculated. In Table XV are given the four metals of the alkali group for which the change in surface tension is appreciable for such minute amounts of dissolved substance, the lowering of surface tension which they produce, and their ionic charges. In the fourth column are given the calculated values of the lowering of the surface tension from the formula $L = Q/15 + 0.7$, where L represents the lowering of the surface tension and Q the ionic charge.

TABLE XV.

Lowering of Surface Tension of Mercury and Ionic Charge.

| Element | Q | L obs. | L calc. |
|---------|------|----------|-----------|
| Na | 15.7 | 1.75 | 1.75 |
| K | 39.6 | 3.65 | 3.34 |
| Rb | 91.2 | 6.8 | 6.78 |
| Cs | 142. | 10.4 | 10.17 |

RELATION OF SPECIFIC GRAVITY TO IONIC CHARGES

The specific gravity of the elements of a given group usually increases with the atomic weight, whether the elements have a positive or negative charge. Since this is also true of the magnitude of the ionic charges, which are approximately proportional to the square root of the atomic weight, there must be, in general, an increase of specific gravity when there is an increase of ionic charge, though possibly not for the same reason.

When we consider compounds made up of positive and negative ions, it seems probable that the specific gravity will be influenced by the magnitude of the attraction between these ions. This is shown in an article in *Physical Review*, N. S., 1, 215 (1913).

That the densities of salts of similar elements are related to the charges of their ions may be seen in their relations to the resultant molecular charges (the algebraic sum of the ionic charges) of their molecules. When the densities of the halogen salts and the sulphates of calcium, strontium and barium are compared with their respective molecular charges, the salts are found to be arranged in their appropriate groups with reference to both their positive and negative ions. This is shown in Table XVI, and, graphically, in Figure 8.

TABLE XVI.
Relation of Densities to Molecular Charges.

| Salt | Mol. Chg. | Sp. g. | Salt | Mol. Chg. | Sp. g. |
|-------------------|-----------|--------|-------------------|-----------|----------|
| CaCl ₂ | — 54.2 | 2.26 | CaI ₂ | —225. | 4.9 (?)* |
| SrCl ₂ | — 2. | 3.05 | SrI ₂ | —187.8 | 4.41 |
| BaCl ₂ | + 44.8 | 3.88 | BaI ₂ | —141. | 4.92 |
| CaBr ₂ | —133. | 3.32 | CaSO ₄ | — 68.4 | 2.96 |
| SrBr ₂ | — 95.4 | 3.96 | SrSO ₄ | — 30.8 | 3.70 |
| BaBr ₂ | — 48.6 | 4.78 | BaSO ₄ | + 16. | 4.33 |

* The density of CaI₂ is clearly out of relation to that of the other salts in this table. It seems to have been determined but once, viz., by Ruff and Plato, *Berliner Berichte*, 35. As I have shown in the paper in *Physical Review* referred to above, there are reasons aside from the above table for thinking that it should be 3.9 instead of 4.9. It is so used in figure 8.

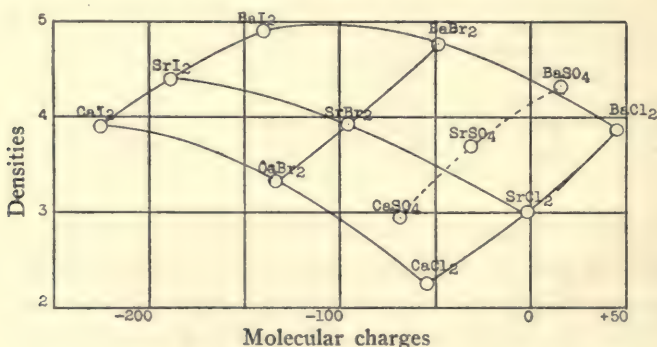


FIGURE 8. Relation of Densities to Molecular Charges.

RELATION OF IONIC CHARGES TO HEATS OF FORMATION

Since the atoms of a compound molecule are held together by the attraction between their opposite charges, or between their electropositive parts and the same electron or electrons, there should be some relation between the heats of formation of different molecules and the charges of their positive and negative ions.

Since in all cases other reactions or solutions are involved in the determination of the heats of formation, and since the magnitudes of these other actions are dependent upon the same ionic charges which determine

TABLE XVII.
Heats of Formation and Products of Ionic Charges

| Salt | QQ' | Ht. of Form. |
|------|------|--------------|
| LiCl | 130 | 187.6 |
| LiBr | 312 | 159.9 |
| LiI | 488 | 122.4 |
| NaCl | 570 | 195.4 |
| NaBr | 1340 | 171.5 |
| NaI | 2040 | 138.2 |
| KCl | 1450 | 211.3 |
| KBr | 3350 | 190.6 |
| KI | 5200 | 160.3 |

the energy changes in the formation of new molecules, it seems impossible to separate the effect of a given charge on one of these phenomena from its effect on the others. Nevertheless, the comparison of the heats of

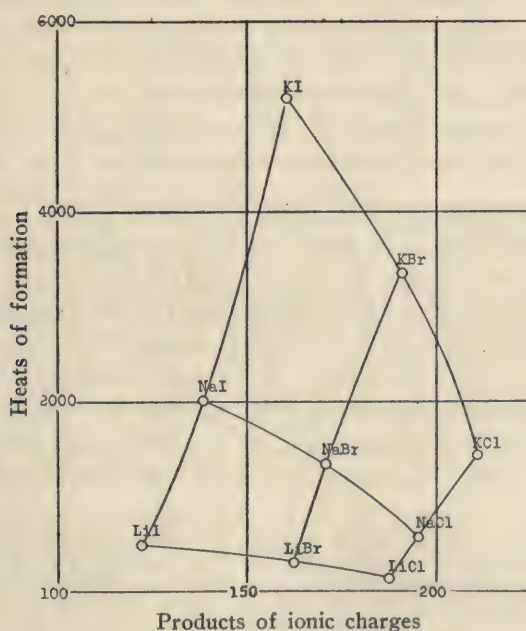


FIGURE 9. Heats of Formation and Products of Ionic Charges.

formation of molecules whose ionic charges may be computed leads to very interesting results, and shows conclusively that the ionic charges are an important factor in determining the heats of combination.

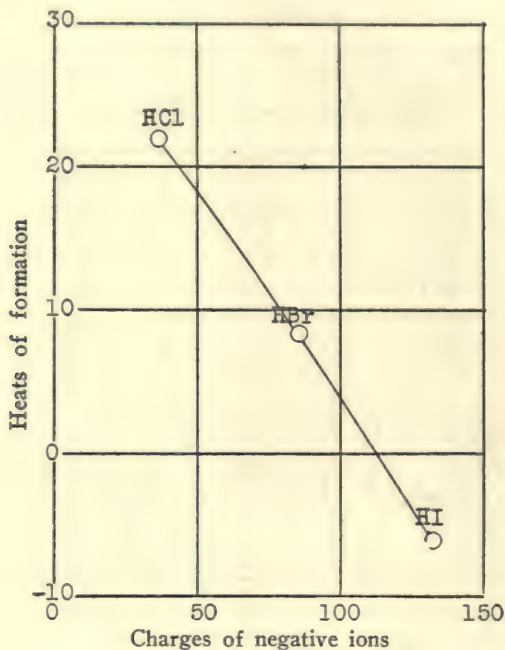


FIGURE 10. Relation of Heats of Formation to Charges of Negative Ion.

Some of these comparisons lead to unexpected results. For example, the heat of combination of an alkali metal with an element of the halogen group is greater the *less* the negative charge of the halogen atom, while, on the other hand, the heat of combination of a given halogen ion with an alkali ion is greater the *greater* the positive charge of the metal.

The heats of formation used here are taken from the tables of Julius Thomsen, and are probably mostly determined in water solution. It may be that the greater attraction of the electronegative ion for water molecules, which is shown in many ways, is to some degree responsible for this result.

In Table XVII the heats of formation of the chlorides, bromides and iodides of lithium, sodium and potassium are compared with the products of their ionic charges. The relation of these products to the heats of formation are also shown graphically in Figure 9.

The relation of the molecular heats of formation to the ionic charges may be shown more plainly by comparing the salts of a given acid with

the charges of the different basic ions, or *vice versa*. Thus if the molecular heats of formation of the chlorides, bromides or iodides of lithium, sodium and potassium are compared with the charges of the positive ions it is seen that there is a linear relation between these quantities. The same is approximately true for the chlorides of magnesium, calcium, strontium and barium.

The relation of the charge of the negative ion to the heat of formation is well shown in the case of the halogen acids, which are all gaseous. The molecular heats of formation of these compounds are given as follows in Thomsen's tables: HCl, 21.98; HBr, 8.4; HI, — 6.1. The relation of these numbers to the charges of the negative ions is shown graphically in Figure 10.

RELATION OF MOLECULAR HEATS OF FORMATION TO THE RESULTANT MOLECULAR CHARGES

We have seen that while there is an undoubted relation between the charges of combining ions and the heats of formation of the molecules which result from their combination, some other factor, probably the atomic dimensions, is also important. It will be seen upon consideration that the *relative*, as well as the *actual*, magnitudes of the combining charges should also play a part. In general, it is assumed that the attraction between two charged bodies is proportional to the product of their charges, but this can be true only when the bodies are far enough apart that the distribution of their charges cannot influence the result and when there are no other bodies near upon which charges may be induced. Thus, two similarly electrified bodies, one of which has a greater charge than the other, may attract each other at small distances and repel each other when at greater distances.

Again, in the case of reactions which take place in water solutions the heat of combination must depend upon the difference in the attractions of the electrified ions for each other and their attractions for the surrounding water molecules. It has already been suggested that water molecules have a small resultant positive charge. If this assumption be correct, the stronger the resultant negative charge of the molecule which is formed in water the smaller the proportion of its total electrical field which will be between its positive and negative ions, and the greater the proportion between its negative ion and the surrounding water. It would seem that the more nearly equal are the charges of the combining ions and consequently the more nearly neutral the resulting molecule, the greater the attraction between them in proportion to their magnitudes.

That there is such a correspondence between the molecular heats of formation and the resultant molecular charges in the compounds whose heats of formation we have been considering may be seen from Table XVIII. The same relations are shown graphically in Figure 11.

TABLE XVIII.
Molecular Heats of Formation and Molecular Charges.

| Salt | Mol. Chg. | Ht. of Form. | Salt | Mol. Chg. | Ht. of Form. |
|------|-----------|--------------|------|-----------|--------------|
| KCl | + 3. | 211.3 | LiBr | — 81.3 | 159.9 |
| NaCl | — 20.8 | 195.4 | KI | — 93. | 160.3 |
| LiCl | — 32.9 | 187.6 | NaI | —117. | 138.2 |
| KBr | — 43.3 | 190.6 | LiI | —129. | 122.4 |
| NaBr | — 69.2 | 171.5 | | | |

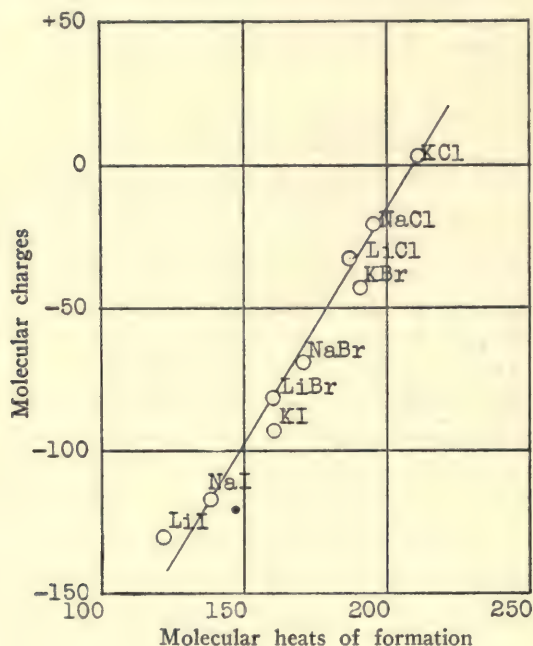


FIGURE 11. Relation of Molecular Heats of Formation to Molecular Charges.

IONIZATION OF GASES AND IONIC CHARGES

In *Royal Society Proceedings*, A 79, pp. 227 and 231 (1907), Klee-man gives the results of an experimental comparison of the relative amounts of ionization produced in different gases by the alpha, beta and gamma rays of radioactive substances. In his tables, the ionization constant of air is taken as unity. Four of the gases whose ionization constants he determines are elements whose ionic charges have been calculated from their ionic mobility in electrolysis. These elements and their ionization constants for the various radiations are given in Table XIX.

TABLE XIX.
Ionization Constants.

| Element | α -rays | β -rays | γ -rays |
|---------|----------------|---------------|----------------|
| H | .175 | .18 | .18 |
| Cl | 1.16 | 1.44 | 1.44 |
| Br | 1.72 | 2.76 | 2.81 |
| I | 2.26 | 4.10 | 4.50 |

It will be seen that while the ionization produced by the β and γ -rays is practically the same, that produced by the α -rays is much less. In either case, however, there is a constant relation between the magnitude of the negative charge and the ionization produced by the radiation. This relation is shown graphically in Figure 12, where Curve I shows the relation between the ionic charge of the element and the mean ionization produced by the β and γ -rays, and Curve II shows the same relation for the α -rays.

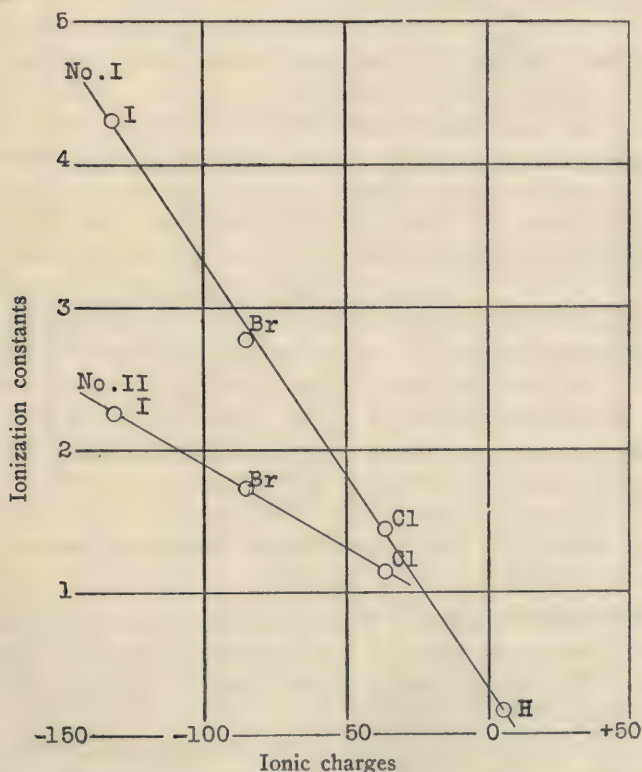


FIGURE 12. Relation of Ionization of Gases to Ionic Charges.

HEAT OF IONIZATION AND IONIC CHARGES

It is assumed in the chemical theory of Nernst and Ostwald that "The neutralization of any strong base by any strong acid must liberate the same quantity of heat," namely, 13,700 calories per gram equivalent. When less than this quantity of heat is liberated by the reaction, it is assumed that the deficiency was required to ionize the reagents before they could combine. That is, the ions acquire potential energy to this amount on being separated from their partners. In case the heat of neutralization is greater than 13,700 calories, it is assumed that the ions actually liberate heat in the process of separation, which implies that before separation there was a repulsion between them. In this case, the heat of ionization is said to be negative.

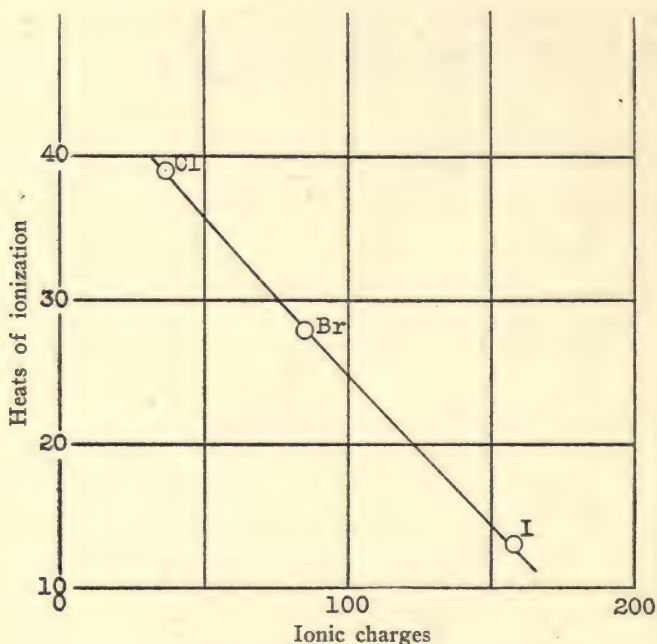


FIGURE 13. Relation of Heats of Ionization to Ionic Charges.

Landolt and Boernstein's Tables give the heats of ionization of a number of elementary substances as calculated by Ostwald. Among these are three of the halogen group, whose heats of ionization are given as follows: chlorine, + 39; bromine, + 28; iodine, + 13. From the point of view of this discussion, this means that the heats of neutralization are not all the same, notwithstanding the Nernst-Ostwald theory, and that the reaction of iodine with a base actually liberates more heat than does the

reaction with bromine, and that the reaction with bromine liberates more heat than does the reaction with chlorine. This should be expected, since we have already seen that the heats of formation of the chlorides, bromides and iodides are in the order here given for the heats of ionization. In fact, the differences between the heats of ionization as given by Ostwald are almost the same as the differences between the heats of formation of the hydrogen acids of these elements as given by Thomsen.

We should accordingly expect these so-called heats of ionization to bear a linear relation to the ionic charges of the elements. That such is the case may be seen from Figure 13.

MOLECULAR CHARGES AND SOLUBILITY

We have already observed that in the case of elementary ions the solubility in water is proportional to the ionic charge. We have also seen that the cohesion between molecules bears a definite relation to the resultant molecular charge. It would seem to follow as a necessity that the solubilities of molecules which are not dissociated into ions should be related to their resultant charges.

Since, however, this resultant charge will be differently distributed in molecules of different kinds, the magnitude of the resultant charge will be only one of the factors which determine the cohesion for other molecules. In molecules of the same general structure we should expect the resultant charge to be the principal factor in determining the relative cohesion of different molecules for the solvent. We should accordingly expect the solubility in a given liquid of salts of similar constitution to be proportional to their resultant molecular charges.

This expectation is based upon the assumption that the molecules of the solute are not dissociated in the solution. When ionization takes place in the solution, the cohesion must depend upon the attraction between the dissociated ions and the solvent. Owing to the fact that we can compute by our method the molecular charges of only those substances which dissociate into their ions in water solutions, we cannot expect a close agreement between the solubilities as calculated from the molecular charges and the actual solubilities, which are to a greater or less degree dependent upon the degree of dissociation. Still, the relation of solubility to resultant molecular charge is striking enough to justify our hypothesis as to the nature of solution.

In Table XX are given the resultant molecular charges and the solubilities in water of a number of salts. The solubilities are taken from "Seidell's Solubilities of Inorganic and Organic Substances." It will be seen from the table that the solubilities are quite roughly proportional to the resultant charges. The abnormally high solubility of rubidium bromide is not explained.

TABLE XX.
Molecular Charges and Solubilities.

| Molecule | Charge | Solubility | Molecule | Charge | Solubility |
|----------|--------|------------|--------------------|--------|------------|
| LiF | — 9.6 | .27 | KBr | — 44. | 53.5 |
| LiCl | — 31. | 67. | KI | — 90. | 127.5 |
| LiBr | — 79. | 143. | RbCl | + 54. | 77. |
| LiI | —125. | 151. | RbBr | + 6. | 89.6 |
| NaF | + 2. | 4. | CsCl | +103. | 161.4 |
| NaCl | — 19. | 35.6 | CsI | + 9. | 1. |
| NaBr | — 67. | 79.5 | NH ₄ Cl | — 17.5 | 29.4 |
| NaI | —113. | 158.7 | RbI | — 40. | 138. |
| KCl | + 3.6 | 27.1 | | | |

Rubidium iodide is not given in Seidell's tables, and the above value is taken from Landolt and Boernstein's tables. Its solubility, as well as that of rubidium bromide, seems abnormally high.

It will be seen that if the salts of a given metal are considered, the solubilities increase with the charge of the negative ion, and this law holds for the rubidium salts as well as the others. Thus for the halogen salts of rubidium and potassium the solubilities as given in L. and B.'s tables are compared with the charges of their negative ion in Table XXI.

TABLE XXI.
Solubility and Charge of Negative Ion.

| Salt | Sol. | Salt | Sol. | Chg. of—Ion |
|------|------|------|-------|-------------|
| RbCl | 77 | KCl | 27.6 | 36.5 |
| RbBr | 98 | KBr | 53.5 | 84.9 |
| RbI | 138 | KI | 127.5 | 132.5 |

INFLUENCE OF THE MOLECULAR CHARGE OF THE SOLVENT UPON THE SOLUBILITY OF A GIVEN SUBSTANCE

In the preceding pages we have seen that the solubility of various salts in water is related to the molecular charge of the salt. It is also possible to show the change in the solubility of a given substance due to changing the electrical charges of the molecules of the solvent.

In a paper by G. Just, entitled "Loeslichkeit von Gasen in organischen Loesungsmitteln,"¹⁸ is given a table of the solubility of CO₂ in a large number of organic liquids. Among these solvents are benzole and its halogen derivatives, chlorbenzole, brombenzole and iodbenzole. These solubilities show that the substitution of a halogen ion for a hydrogen ion in the benzole molecule invariably decreases the solubility of CO₂ in the

¹⁸ *Zeitschrift für physikalische Chemie*, 37, 354.

liquid. This should follow from the fact that CO_2 is apparently a negatively charged molecule, and the benzole molecule is made less electro-positive by the substitution of a negative halogen ion for a positive hydrogen ion.

Since the halogen ions have charges of different magnitudes, it must follow from this line of argument that the greater the negative charge of the substituted ion the less should be the solubility of CO_2 in the liquid. That this is the case may be seen from the following data taken from Tabelle 1 in Just's paper. That the solubility not only decreases as the negative charge of the substituted ion increases, but that the two quantities bear a nearly linear relation to each other, may be seen from Figure 14, in which the decrease of solubility due to the substitution of the halogen ions is shown by the ordinates and the charges of the substituted ions by the abscissas.

TABLE XXII.
Solubility of CO_2 in Benzole and Its Derivatives.

| Solvent | Solubility of CO_2 | Decrease of Solubility | Charge of —Ion. |
|---------------------------------|-----------------------------|------------------------|-----------------|
| C_6H_6 | 2.425 | | |
| $\text{C}_6\text{H}_5\text{Cl}$ | 2.265 | .16 | — 36.5 |
| $\text{C}_6\text{H}_5\text{Br}$ | 1.842 | .583 | — 84.9 |
| $\text{C}_6\text{H}_5\text{I}$ | 1.301 | 1.124 | —132.5 |

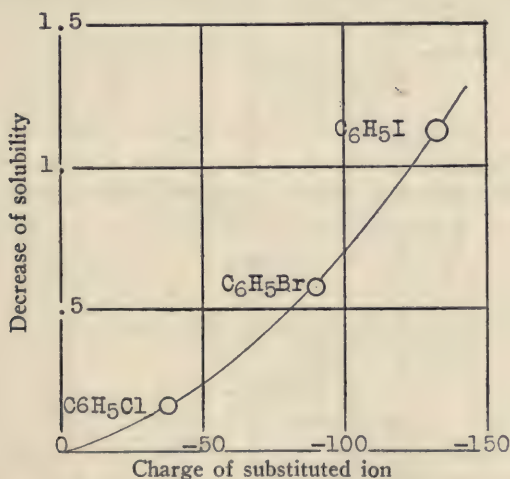


FIGURE 14. Decrease of Solubility in Benzole Derivatives with an Increase in the Negative Charge of the Substituted Ion.

EXPANSION OF SALTS IN WATER SOLUTION COMPARED WITH THEIR
RESULTANT MOLECULAR CHARGES

Salt solutions in general have higher expansion coefficients than water, and those salts which produce the greatest volume contraction on solution have the highest expansion coefficients in solution. Since the expansion coefficients and the volume contractions on solution increase or decrease together, there should be a relation between the resultant molecular charge of a salt and the expansion coefficient of its solution. That such is the case may be seen from Table XXIII, in which the expansion coefficients in solution of the halogen salts of the barium group are compared with their resultant molecular charges.

TABLE XXIII.

Expansion of Dissolved Salts Compared With Their Molecular Charge.

| Salt | Exp. Coef. | Mol. Chg. | Salt | Exp. Coef. | Mol. Chg. |
|-------------------|------------|-----------|-------------------|------------|-----------|
| MgCl ₂ | 22 | — 54.3 | SrBr ₂ | 182 | — 95.4 |
| CaCl ₂ | 105 | — 39.6 | BaBr ₂ | 201 | — 48.6 |
| SrCl ₂ | 142 | — 2 | MgI ₂ | 158 | —240 |
| BaCl ₂ | 165 | + 44.8 | CaI ₂ | 236 | —225 |
| MgBr ₂ | 70 | —147.6 | SrI ₂ | 268 | —187.3 |
| CaBr ₂ | 153 | —133 | BaI ₂ | 288 | —141 |

The expansion coefficient due to the dissolved salt is determined by subtracting the expansion of water from that of the salt solution for the

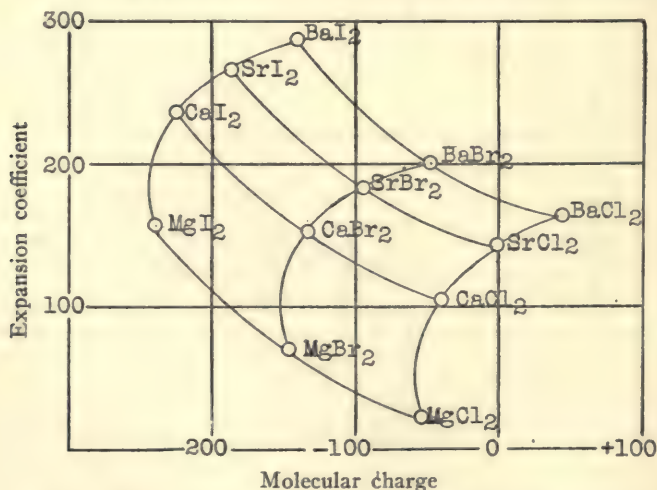


FIGURE 15. Relation of Expansion of Salts Dissolved in Water to their Molecular Charges.

same temperature range. The increase in volume is for the interval between 19.5 degrees and 40 degrees, and is taken from Landolt and Boernstein's tables. The molecular concentration is 20 gram-equivalents of the salt in 10,000 grams of water. The increase in volume is given in hundred-thousandths of the volume taken at 19.5 degrees.

It will be seen that for a given group of either the electropositive or electronegative ions there is a plain relation between the two quantities given in the table. This relation is more easily seen when expressed graphically, as in Figure 15.

If Figure 15 be compared with Figure 8, a striking resemblance will be seen. This shows that a definite relation must exist between the specific gravities of these salts and their expansion coefficients in water solution.

Atomic Charges and Serial Numbers of the Elements

Up to the present stage of this discussion the writer has attempted to show merely that the quantities which have been called ionic charges, and which have been calculated from the mobility of the ions and the atomic weights, are, within groups of similar elements, closely related to all the properties of bodies which depend upon cohesion. It seems, however, that the cohesion between atoms and molecules depends upon the distribution of their positive and negative charges as well as upon their magnitude, and accordingly the regularities which we have observed between cohesion magnitudes and ionic charges are confined more or less closely to recognized chemical groups of atoms.

At the time when attention was first called to the characteristic charges of the atoms which are here being considered,¹⁴ it was generally believed by physicists and chemists that all elementary ions carry electrical charges which are small, integral multiples of the charge on the hydrogen ion. While this opinion seems still to be the prevailing one, there are evidences of a strong drift of opinion toward the existence of characteristic atomic charges which bear some definite relation to the atomic weight or to the serial number of the respective atom.

In 1911, Rutherford¹⁵ and Barkla¹⁶ concluded from the scattering of α -particles and of X-rays that the elementary atom carries a positive charge which is proportional to half its atomic weight.

In a paper entitled, "Untersuchungen ueber das System der Grundstoffe," (Lund, 1913), Rydberg has undertaken to show that the properties of the elements which determine their positions in the periodic

¹⁴ *Physical Review*, 32, 512 (May, 1911).

¹⁵ *Philosophical Magazine*, 21, 669.

¹⁶ *Ibid.*, 21, 648.

series may be inferred from the numbers which represent the order of their occurrence in this series. Thus he says.¹⁷

In the system of Mendelejeff all the elements are arranged in a single series, and each element is distinguished from all the others by its place in this series. This signifies that *a single independent variable suffices to completely determine each element*. According as a quantity to be determined varies continuously or discontinuously must the independent variable pass through the continuously increasing series of all numbers or the discontinuous series of the positive whole numbers. In the case before us one cannot doubt that the properties of the elements vary discontinuously from element to element. Continuous variation in the properties of the elements may, indeed, occur, but only in consequence of a continuous change in temperature, pressure, and the like, of the same element. Between the individual elements there is no continuous transition.

We are accordingly led to the adoption of the series of the positive whole numbers as the independent variable for the system of the atoms.

Rydberg then undertakes to show that the characteristics of the atoms upon which the periodic law was based may be calculated, so far as their magnitudes are concerned, by means of mathematical relations between their atomic numbers in the periodic series. He does not propose any physical explanation of these numerical relations.

Such a physical explanation is suggested in a discussion by A. Van den Broek in a paper entitled, "Die Radioelemente, das periodische System und die Konstitution der Atome."¹⁸ Van den Broek concludes that in general the atomic weight of the elements changes from atom to atom in the periodic series by about two units, and that the deviations from this law are accidental. He also assumes that each change in atomic weight is accompanied by the gain or loss of a definite electric charge; hence the positive sub-atom or nucleus of an elementary atom should carry a charge proportional to the serial number of the atom in the chemical series. This hypothesis gives a physical significance to the atomic numbers which Rydberg regards as the descriptive characteristics of the elements.

Previous to these papers by Rydberg and Van den Broek, the present writer had published a paper on "The Significance of the Periodic Law,"¹⁹ in which he said:

The discovery of radioactivity and the successive disintegrations of the uranium and thorium atoms seem to have shown us how these atoms were originally put together. In this process we see one elementary atom changing into another of lower atomic weight by releasing one or more alpha particles or one or more negative electrons, or in some cases, perhaps, by giving off both an alpha

¹⁷ Translation by present writer.

¹⁸ *Physikalische Zeitschrift*, **14**, 32 (1913).

¹⁹ *Journal of American Chemical Society*, **33**, 1349 (August, 1911).

particle and an electron in a single change. Since the electron has but little, if any, influence upon the atomic weight, we find these successive atoms differing in atomic weight by four or eight, or in case where only an electron is set free we may have two successive atoms with the same atomic weight but with different chemical properties.

Since the disintegration products of uranium seem to fall into their proper positions in the periodic series and to have properties analogous to the other members of their periodic groups, radium, for example, showing the characteristic properties of the barium group, and emanation forming an inert gas of the argon group, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight.

A difficulty in constructing the elementary series in this way arises from the fact that the atomic weights of successive elements do not increase by four or by multiples of four. This difficulty is largely overcome for a considerable part of the series by assuming two parallel lines of development, one line starting from helium and one from lithium.

Such an arrangement of the periodic series was then shown, putting alternate groups from Mendelejeff's series into separate series, and placing the triplet groups of metals, iron, nickel, cobalt, ruthenium, rhodium, palladium and osmium, irridium, platinum in the gaps in the group of inert gases. The paper then says:

Starting with helium, it will be seen that the series is regular up to and including iron, Be being the only element whose atomic weight does not conform to our requirements, its atomic weight being nine instead of eight. With the occurrence of the triplets Fe, Ni, Co, the orderly arrangement is broken up, though the preponderating influence of the quantity four may still be observed. Thus the increase in atomic weight from cobalt to rhodium is 44 and from rhodium to osmium 88. If the lowest atomic weight in a column be subtracted from the highest above the first series of missing elements, we have $\text{Xe} - \text{He} = 124$; $\text{Ba} - \text{Be} = 128$; $\text{Ce} - \text{C} = 128$, and $\text{Pr} - \text{O} = 124\frac{1}{2}$.

* * * * * *

In the lithium series the agreement with theory is about equally good throughout with that of the helium series. The irregularity begins at about the same atomic weight and is about equally great, though there seem to be more occurrences of six as a difference between two successive atomic weights. In both series these irregularities begin where each group of the series seems to split into two groups, as the group of the alkali metals and the copper, silver and gold group. These irregularities offer a serious difficulty to the acceptance of the theory of atomic development here outlined.

* * * * * *

It is well known that certain fundamental differences seem to exist between the two groups of elements which are here characterized as the helium series and the lithium series. The two series have, in fact, long been separated on the basis of their chemical valency, the elements of the helium series having zero valency or even valencies, while the elements of the lithium series have odd valencies. They have likewise been separated on the basis of their spectra, the elements of the helium series having their spectral series made up of single lines or groups of three,

while the elements of the lithium series have their spectral lines arranged in pairs. From the researches of Sir Norman Lockyer and others on the spectra of the stars, it would seem that in the hottest stars only elements of the helium series are found, several of these elements apparently appearing before any of the lithium elements appear. Thus calcium and iron are said to appear before sodium.

This hypothesis of two periodic series of elements, instead of one, has been adopted and much further developed by W. D. Harkins and his students. If it be accepted, or if the Van den Broek hypothesis of an additional hydrogen charge being added with each increase of one in the atomic number be preferred, there should still be within each group, at least, a close relation between the atomic number and the positive charge of an atom. Whether the total charge, including the charges of the alpha particles or the hydrogen particles and their associated electrons, should be strictly proportional to the atomic numbers cannot be inferred without knowing more about atomic structure, but it would seem that within groups of similar elements this proportionality should hold.

In order to test this hypothesis there is given in Table XXIV a list of all the elements whose ionic mobilities are given in Kaye and Laby's tables, together with their serial numbers and ionic charges, calling the charge of the hydrogen ion 5. In Figure 16 the relations shown in this table are expressed graphically for the monovalent elements.

TABLE XXIV.
Serial Numbers and Atomic Charges.

| Element | No. | Chg. | Element | No. | Chg. |
|---------|-----|------|---------|-----|-------|
| H | 1 | 5 | Br | 35 | 84.9 |
| Li | 3 | 3.6 | Rb | 37 | 91.2 |
| F | 9 | 14.6 | Sr | 38 | 71.5 |
| Na | 11 | 15.7 | Ag | 47 | 91.6 |
| Mg | 12 | 17.3 | Cd | 48 | 83.8 |
| Cl | 17 | 36.5 | I | 53 | 132.5 |
| K | 19 | 39.6 | Cs | 55 | 142 |
| Ca | 20 | 32.5 | Ba | 56 | 119.4 |
| Cu | 29 | 46.7 | Tl | 81 | 212 |
| Zn | 30 | 47.6 | Pb | 82 | 199.4 |

It would seem to follow from the above relation between the serial numbers and the ionic charges that the relative cohesion constants of the elements in a characteristic group whose ionic charges may not be determined by electrolysis may still be inferred from their serial numbers. The helium group of gases furnishes an excellent example of such a characteristic group whose charges cannot be calculated by the method here used.

The melting points and boiling points of these gases are known with

a fair degree of accuracy except in the case of Neon. Van der Waals' constant and the critical temperatures have been calculated from these measurements. Sutherland has shown how to calculate from the viscos-

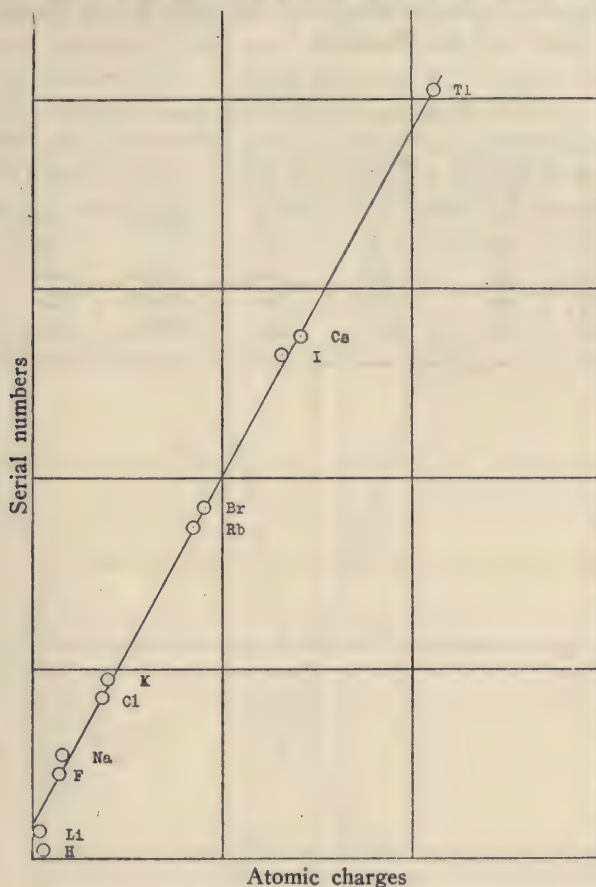


FIGURE 16. Relation between the Serial Numbers and the Atomic Charges of Monovalent Elements.

ity of gases a cohesion factor, "C," which represents the attraction between the molecules (in this case the atoms) of the gas, and Rankine²⁰ has measured the viscosities of these gases and has calculated the value of Sutherland's constant "C" from his measurements. The solubility of these gases in water has been determined by A. van Antropoff.²¹ All of these properties depend upon cohesion and have been shown to vary with the ionic charges in the case of other groups of elements. In Table XXV

²⁰ *Philosophical Magazine*, 21, 45.

²¹ *Royal Society Proceedings*, A. 83, 474.

these constants are given along with the serial numbers of the elements.

If any one of these properties be plotted against the serial numbers, a nearly linear relation will be given. This is shown for the critical temperature in Figure 17, for Sutherland's constant "C" in Figure 18, and for Van der Waals' "a" in Figure 19.

TABLE XXV.
Serial Numbers and Cohesion.

| Element | No. | Melting Point | Boiling Point | Critical Temp. | "a" | "C" | Solubility |
|---------|-----|---------------|---------------|----------------|--------|-----|------------|
| He | 2 | 3 | 4.5 | 4 | .00006 | 70 | .0138 |
| Ne | 10 | 20 (?) | (?) | (?) | (?) | 56 | .0147 |
| Ar | 18 | 85 | 86.9 | 154 | .00259 | 142 | .0379 |
| Kr | 36 | 104 | 121.3 | 210 | .00462 | 188 | .0729 |
| X | 54 | 133 | 164 | 258 | .00818 | 252 | .1109 |

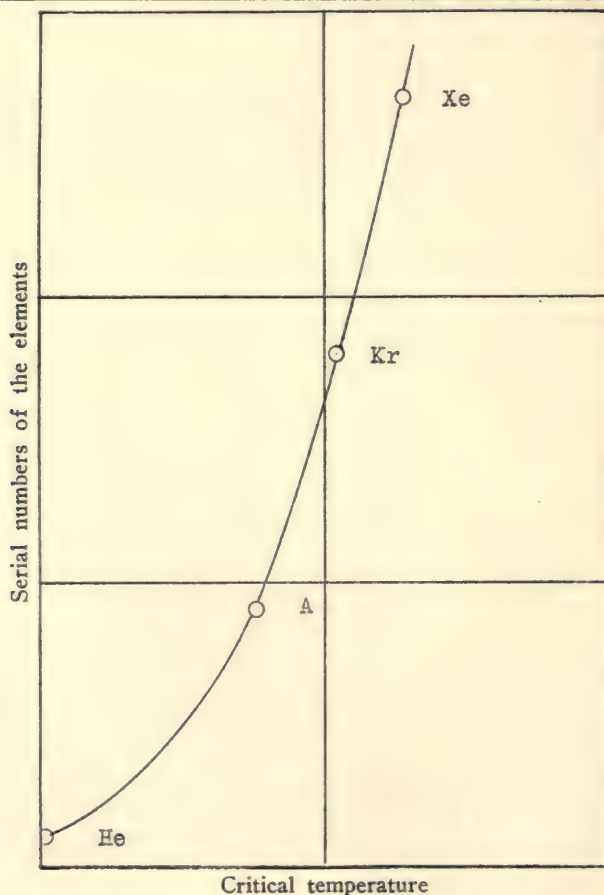


FIGURE 17. Relation of Critical Temperatures to the Serial Numbers of the Elements.

A consideration of the above table, together with Figures 17, 18, and 19, shows very certainly that the properties of the helium gases which depend upon cohesion vary with the serial numbers of the elements. That the same holds true for the other atomic groups we have been considering is shown by the linear relation of their ionic charges to their serial numbers. The fact that these relations do not hold in passing from one group to another indicates that the distribution of positive and negative charges within the atom, upon which cohesion must necessarily depend, is not the same in different groups, and it suggests that it may be this distribution which largely determines the chemical properties of the atoms.

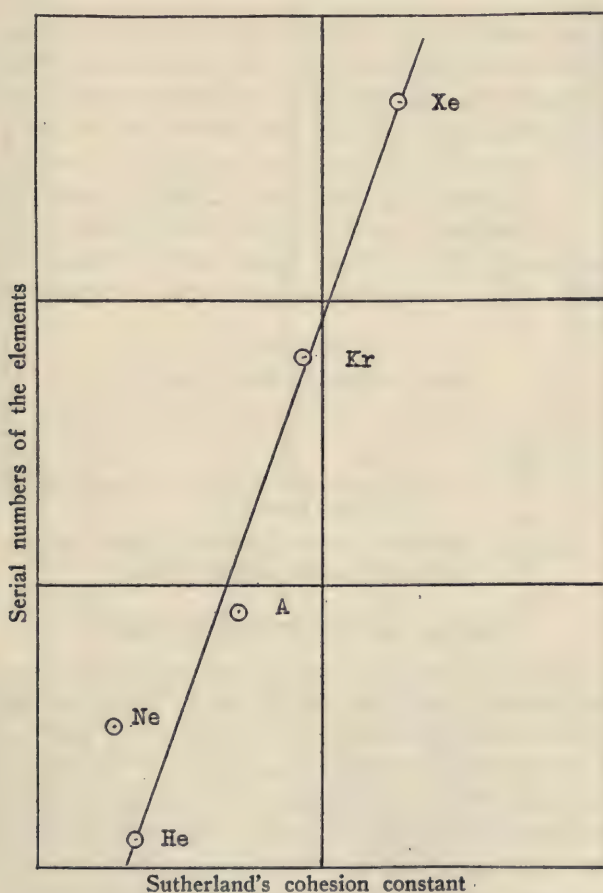


FIGURE 18. Relation of Sutherland's Cohesion Constant to the Serial Numbers of the Elements.

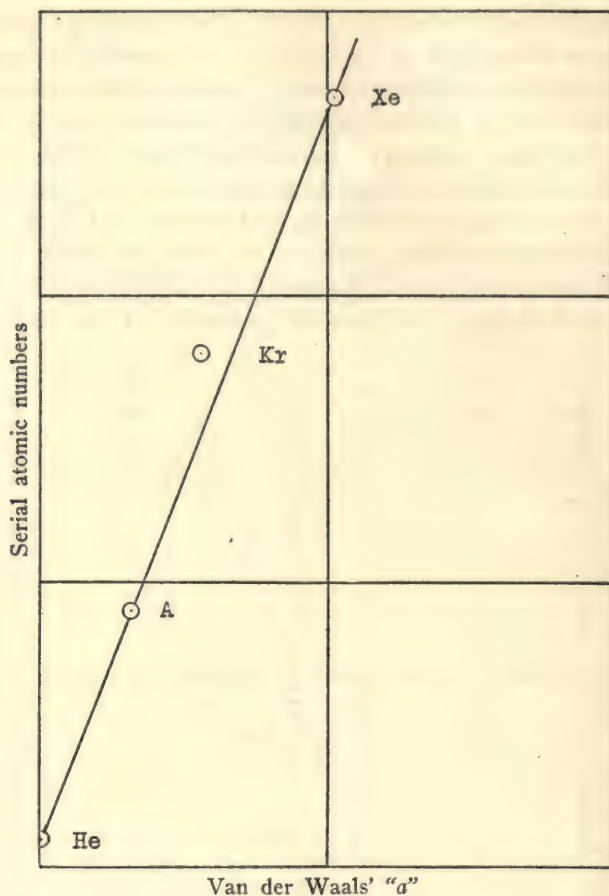


FIGURE 19. Relation of the Cohesion Constant "a" to the Serial Numbers of the Atoms.

Charges of Ions from Hot Metals

It is well known that many metals when sufficiently heated give off both positive and negative ions to the air. Numerous attempts have been made to determine the charges of these ions, but with only moderate success. In a paper by Richardson and Hulbirt²² is given a list of the values of the ratio of charge to mass of the positive ions from ten hot metals. Four of the ten metals gave results unsatisfactory to the authors, while another, gold, gave two values of e/m , one of which was twice as great as the other, and the variations of the values found in different experiments was very great in all cases.

²² *Philosophical Magazine*, 20, 545 (1910).

The six metals whose values of e/m were regarded as approximately correct gave values of this ratio which differed so little among themselves that the authors concluded that the same ion was given off by all; and since the mean value was approximately the value which the sodium ion should give if its charge were equal to the charge of the hydrogen ion, the authors concluded that all the metals used by them contained sodium as an impurity (notwithstanding that they were all metals near the electronegative end of the voltaic series) and that when heated they gave off only sodium ions. They reached this conclusion because they were committed to the view that the charges of the metallic ions given off by hot bodies must always equal some simple, integral multiple of the hydrogen charge.

If this assumption, which has no experimental basis, be disregarded, and their experimental values of e/m be multiplied by their respective atomic masses, a series of experimental values of e are obtained, and these values are related to each other and to their atomic numbers and cohesion constants much in the same way as are the charges of elements of similar groups when calculated from electrolytic data.

Richardson and Hulbirt's values of e/m , the values of e obtained by multiplying these ratios by the atomic masses of their respective elements, and the serial numbers of the elements are given in Table XXVI.

TABLE XXVI.
Charges of Ions From Hot Metals.

| Element | e/m | e | No. | |
|---------|-------|-----|-----|----|
| Pt | 243 | 474 | 78 | |
| Pd | 212 | 225 | 46 | |
| Ni | 239 | 130 | 28 | |
| Au } | 139 | 276 | } | 79 |
| | 280 | 552 | | |
| Ag | 215 | 232 | 47 | |
| Cu | 230 | 146 | 29 | |

The relation between these relative values of e and the serial numbers of their respective elements is shown graphically in Figure 20. It is seen that when, as in the figure, the mean of the two values for gold is used, the relation between the two quantities is shown by a straight line except in the case of platinum, for which this computed value of e seems too high. Another value for platinum, which is marked on the figure by a dot, will be referred to later.

A few other ions have had their charges approximately determined by other methods. For example, in a series of experiments on the

charges carried by positive ions in the case of electric discharge through gases, Sir J. J. Thomson has calculated the value of the ratio e/m for a number of different ions; but owing to the fact that these ions cannot be identified except by means of the ratio determined, their identification must depend upon the assumptions made regarding their charges and they are not adapted to the calculation of ionic charges.

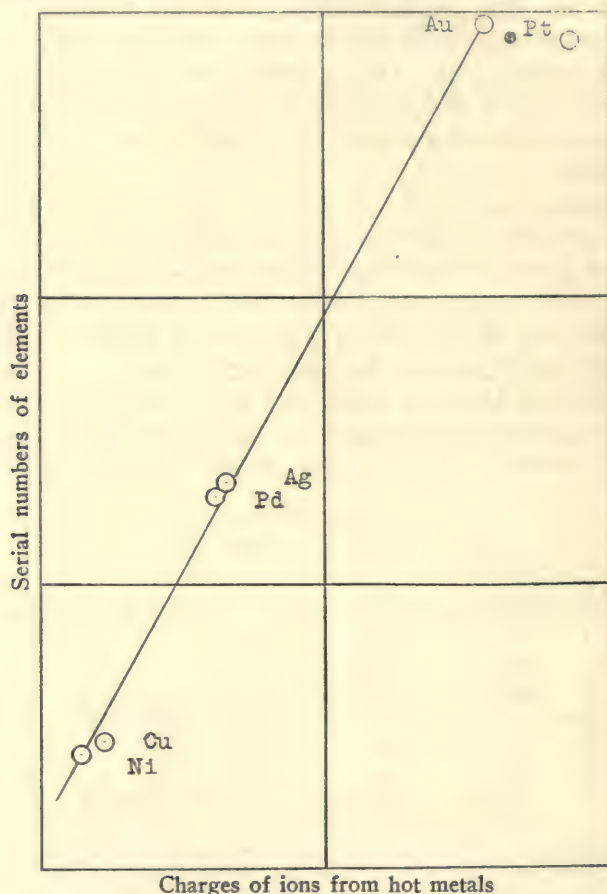


FIGURE 20. Relation of the Charges of Ions from Hot Metals to the Serial Numbers of the Elements.

In Thomson's experiments his highest values of e/m have generally been assumed to belong to the hydrogen ion. Another ion with half this value of e/m , which he has regarded as a hydrogen molecule minus one electron, would seem more likely to be an alpha-particle, which is known to have four times the mass and approximately twice the charge of the hydrogen ion.

In a paper by C. T. Knipp, entitled "Rays of Positive Electricity from the Wehnelt Cathode,"²³ are given values of e/m for a number of positive particles sent off from a red-hot platinum cathode on which is a small speck of calcium oxide. Both kinds of ions mentioned above as having been found by Thomson also appear in Knipp's tube, though his value of the ratio of the supposed hydrogen ion differs from Thomson's value by about 20 per cent. In addition to the ions observed by Thomson, Knipp gives values for two ions which were not observed by Thomson. One of these gave a value of e/m equal to .18 that of the hydrogen ion, and the other gave a value of .044 of the ratio for the hydrogen ion.

The two red-hot metals on Knipp's cathode were calcium and platinum. The values of the charges for calcium and hydrogen ions when calculated by the electrolytic method make the ratio e/m for calcium .18 that for hydrogen, which seems to agree with Knipp's measurements. Knipp's value for his other unknown ion differs by about 10 per cent from the value for platinum taken from Richardson and Hulbirt's data, and would change the relative value of the charge given in Table XXVI from 474 to 431. This point is marked by a dot on the curve in Figure 20, and it will be seen that it lies much closer to the straight line than does the value given by Richardson and Hulbirt's data.

MOBILITIES OF POSITIVE IONS IN FLAMES

When the salts of the alkali metals are heated in a Bunsen flame they are known to give off positive ions. In a study of the Hall effect in flames Erich Marx²⁴ has shown that in a given electrical field the velocities of the positive ions from the chlorides of the alkali metals when sprayed into a Bunsen flame are in the order of their atomic weights. This indicates that the magnitude of their charges must be in that order, since if their charges were all of the same magnitude they would all be impelled by the same force, and the lighter ions would have the higher speeds.

It is also well known that when the salts of the alkali metals are dissociated in a flame, the outer cone of the flame (sometimes known as the mantle of the flame) is colored by the positive ions of the salts. T. P. Irving²⁵ has shown that when the outer cone is well separated from the inner cone of the flame it may be strongly deflected toward the negative side of an electric field, thus showing definitely the electropositive character of the ions which give color to the flame. Irving has also determined the order of the relative deflection of the alkali ions in a given electrostatic field, and found this order to be caesium, rubidium, potassium,

²³ *Philosophical Magazine*, **22**, 926 (1911).

²⁴ *Annalen der Physik*, **2**, 798 (Aug., 1900).

²⁵ *Physical Review*, **29**, 248 (1909).

sodium, lithium. Since the ions were presumably carried upward by the hot gases of the flame at approximately the same speed in all cases, this indicates definitely that the mobility of the ions in flames when in an electrical field is in the same order as their mobilities in water solutions. In this case the differences in speeds cannot reasonably be attributed to a difference in hydration.

A similar order holds in the conductivities of the vapors of these metals in flames. The electrical conductivities of flames containing as nearly as possible equal concentrations of the vapors of these metals are given as follows: caesium, 116; rubidium, 82; potassium, 64; sodium, 8.5; lithium, 2.5. These numbers are in the same order and are roughly approximately of the same value as the charges of these ions calculated from electrolytic data.

It seems to the writer that what proofs we have been able to gather concerning the magnitude of the charges of ions from hot metals, while not as conclusive as the evidence from electrolytic data, are strongly corroborative of that evidence.

POSITIVE ATOMIC CHARGES AND RADIATION

ON THE NATURE OF ELECTROMAGNETIC RADIATION

All kinds of ether radiation are now believed to be set up by the oscillations of electric charges, either upon conducting bodies or in the free ether.

The forms of radiation which we call light and X-rays seem to be produced by the oscillations of single electrons rather than groups of electrons. Since these oscillations are strictly periodic in character, and since a periodic oscillation can be set up only when a restraining force acts upon the oscillating body or particle to bring it back to a position of equilibrium, electrons can give off periodic radiations only when they are oscillating under the restraint of a central force.

While there are many possible forms of periodic oscillations there seem to be only two simple forms which are capable of being produced by electrons in such a system as the chemical atom seems to be, namely, rectilinear, simple-harmonic vibrations, and elliptical or circular orbital oscillations. Either of these kinds may be made to account for many of the phenomena of visible radiation, but it is believed that the Zeeman phenomenon can be explained only on the hypothesis of an orbital oscillation.

Since the only known forces which may act upon moving electrons are either electric or magnetic forces, it seems reasonably certain that visible radiation is produced by electrons oscillating periodically in either an electric or a magnetic field.

The only known type of electron oscillation capable of being set up by a magnetic field is that of an orbital revolution about the magnetic lines of force. An orbital revolution may also be set up about a positive electric charge. A rectilinear, simple-harmonic motion could not be set up in an ordinary electric field, since such a vibration requires a central force which increases with the distance of the vibrating body from the center of its path, while an electric force decreases as the square of the distance from the attracting charge increases. The only kind of electric force capable of sustaining rectilinear electron vibration is apparently the purely imaginary kind proposed by Sir J. J. Thomson, where the vibrating electron is assumed to be located within a sphere of uniformly distributed positive electricity (whatever that may mean), and within such a sphere of positive electricity only a single vibration period would be possible. Since it is believed that single atoms may give off vibrations of many

different periods, the Thomson atom is plainly incapable of accounting for visible radiation and for X-rays.

Since the chemical atom is known to be made up of positive ions and electrons, the electrons are necessarily in an electric field so long as they are attached to the atom, and whatever oscillations they may make would seem to be necessarily under the constraint of this field. If the positive charge of an atom may be regarded as located at a single point, it would seem that the only kind of oscillation possible to an electron attached to such an atom would be an elliptical or circular revolution about the positive charge. Such a revolution would give rise to ether waves whose frequencies would coincide with the frequencies of revolution of the radiating electron.

The kind of radiating atom suggested above has already come into favor from other considerations, so that probably the most common conception of an atom at the present time is that of a central positive nucleus in which is located most of the inertia of the atomic system and about which one or more electrons are, or may be, in revolution. This hypothetical atom is generally known as the Rutherford atom, but it has been independently proposed by a number of physicists, and Lodge has suggested that it be called the "Astronomical Atom".

If we regard atoms as planetary systems consisting of a positive central charge and revolving electrons we are unable to account for the same fixed periods of revolution in atoms of the same element. If there were only a single electron revolving about a positive nucleus it might have, within very wide limits, any period of revolution. The only necessary conditions for equilibrium of the system are that $mv^2/R = Qe/R^2$, where m = the mass, e , the charge, v , the orbital velocity and R the orbital radius of the electron and Q = the magnitude of the central positive charge. Since these conditions could permit the electron to be located anywhere outside the positive charge and within its field of attraction, we can see no reason for the selection of any one vibration period rather than another.

The difficulty is still greater if we think of a number of electrons located at different distances outside the central charge. In this case, each revolving electron reduces the effective central charge for all electrons whose orbits lie outside its own, and hence each electron revolves about a different central charge. Instead of the two possible variables in the above equation, v and R , we now have three, v , R and Q , even if we say nothing about the perturbations produced by the reciprocal repulsions of several electrons revolving about the same central charge at the same time, if, indeed, the different spectral lines of an atom are all produced at the same time.

Up to the present time, no one has been able to compute by means of any known laws of electrodynamics a natural period for one or more electrons revolving about a central positive nucleus.

There have, however, been discovered two empirical equations of the discontinuous character suggested by the spectra of elements. Both of these have been found to apply to X-rays, and one of them to visible radiation. One has a discontinuity based upon the Planck radiation factor, h , and the other upon the serial numbers of the elements, upon which, as we have seen, the atomic charges seem also to be based.

With regard to the Planck constant, it has been found that when electrons are expelled from metals under the stimulus of ultra-violet light their speeds depend not at all upon the intensity of the exciting light, but only upon its vibration frequency; and that the speeds of the electrons after leaving the metals are such that their kinetic energy may be calculated from the equation $\frac{1}{2}mv^2 = \nu h - b$, where h is the Planck radiation factor, ν is the vibration frequency of the incident light and b is a small quantity which is constant for a given metal. b is believed to be the quantity of kinetic energy lost by the electron in breaking away from the metal surface, and is taken as a measure of the contact electromotive force, or what Bennett and Cavallo called the affinity of the metal for the electric fluid. If this be the true explanation of the quantity b , then the electron before it escaped from the surface must have had a speed such that its kinetic energy could be computed from the equation $\frac{1}{2}mv^2 = h\nu$. If this kinetic energy is derived from the energy of orbital revolution of the electron while associated with its atom, which seems to be the only possible explanation of it, then at the instant of its escape from its atom its speed must have been such that $mv^2/R = Qe/R^2$ while $\frac{1}{2}mv^2 = h\nu$.

It has been found that the equation $\frac{1}{2}mv^2 = h\nu$ applies also to electrons which are expelled from metals under the stimulus of X-rays, and that it applies in the inverse order to X-rays induced by the impact of electrons upon metals, as in the ordinary X-ray tube. It seems to follow that whenever the kinetic energy of moving electrons is transformed into the energy of periodic ether vibration, or *vice versa*, the kinetic energy of the electrons is related to the vibration frequency of the radiation by the equation $\frac{1}{2}mv^2 = h\nu$. This would seem to indicate that the exchange of energy between the electrons in an atomic system and the vibrating ether is a resonance phenomenon, and that the orbital period of the electron must be the same as the vibration period of the radiation.

If our assumptions are correct, we accordingly have two simultaneous equations of motion which may be applied to a revolving electron, namely, $\frac{1}{2}mv^2 = h\nu$ and $mv^2/R = Qe/R^2$. We may also write for the orbital velocity of the revolving electron $v = 2\pi R\nu$, giving us three equa-

tions by means of which we may express any one of the variables, Q , R , v and ν , in terms of one of the others and of known quantities. So, also, since the wave-length of the radiation $\lambda = c/\nu$, where c = the velocity of light, we may use the wave-length instead of the frequency, if desired.

We then have as fundamental equations,

$$(1) \quad mv^2/R = Qe/R^2 \text{ and } mv^2 = Qe/R.$$

$$(2) \quad mv^2 = 2h\nu = 2hc/\lambda.$$

$$(3) \quad v = 2\pi R\nu.$$

The best known values for h , e , m and c are as follows:

$$h = 6.55 \cdot 10^{-27}.$$

$$e/m = 1.765 \cdot 10^7 \text{ E. M. U.}$$

$$e = 4.774 \cdot 10^{-10} \text{ E. S. U.}$$

$$c = 2.9989 \cdot 10^{10}.$$

$$(4) \quad \text{Then } Q = h\nu/e\pi = 4.367 \nu \cdot 10^{-18}.$$

$$(5) \quad v^2 = 2hc/m\lambda = 4.357 \cdot 10^{10}/\lambda \text{ and } v = 6.60 \cdot 10^5/\sqrt{\lambda}.$$

$$(6) \quad \text{From (4) and (5) } Q = \frac{h}{e\pi} \sqrt{2hc/m\lambda} = 2.882 \cdot 10^{-12}/\sqrt{\lambda}.$$

$$(7) \quad \text{From (1) and (4), } Rv = h/m\pi = 2.312.$$

$$(8) \quad \text{Also, } R/\sqrt{\lambda} = 3.503 \cdot 10^{-6}.$$

Among other quantities, the above equations enable us to calculate the orbital radius and the central charge of a radiating electron from the wave-length or the vibration frequency of its radiation. As regards the orbital radius, we have no other method of measuring it, and we can only inquire if our equation gives relative values that are in agreement with the relative atomic radii calculated by other methods. This the writer has already done in a paper in *The Astrophysical Journal*, 44, 201 (Nov., 1916).

Since, from our equation $R/\sqrt{\lambda} = 3.503 \cdot 10^{-6}$, there must be as many orbital radii as there are lines in the spectrum of an element, it becomes necessary to select corresponding radii for the different elements if we are to compare them with radii calculated from other considerations. In the paper mentioned above, this was done by selecting the radii corresponding to the convergence wave-lengths in similar spectral series.

It is well known that in many elements there are certain groups of spectral lines whose wave-lengths may be calculated by means of a more or less simple mathematical formula. The lines of such a series must certainly belong to a single vibrating system, while it seems probable that when there are two or more such series for a single element the different series belong to different atomic systems. All the formulae which have thus far been used for calculating the wave-lengths of the lines of a series converge to a shortest possible wave-length in the series, and this convergence wave-length should give the least possible radius of revolution for an electron in that particular atomic system.

In the paper above mentioned the radii calculated from these convergence wave-lengths for a number of similar spectral series are

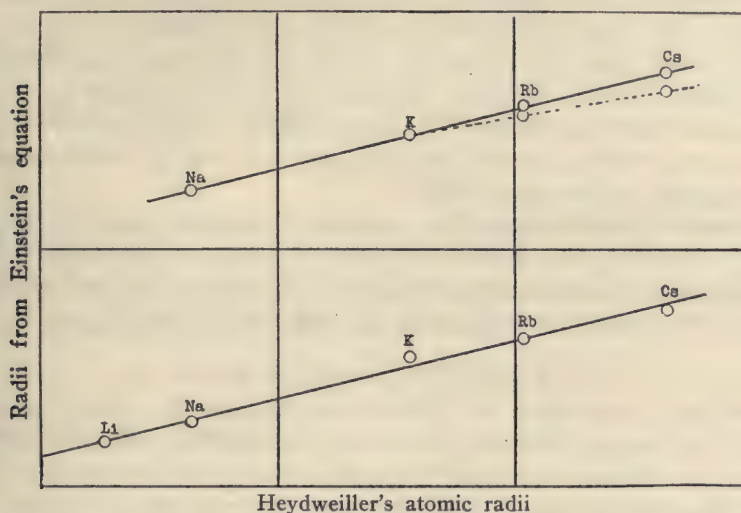


FIGURE 21. Relation between Heydweiller's Atomic Radii and Radii from Einstein's Equation

compared with the cube root of the atomic volumes and with a set of atomic radii calculated by A. Heydweiller²⁶ on the assumption of the

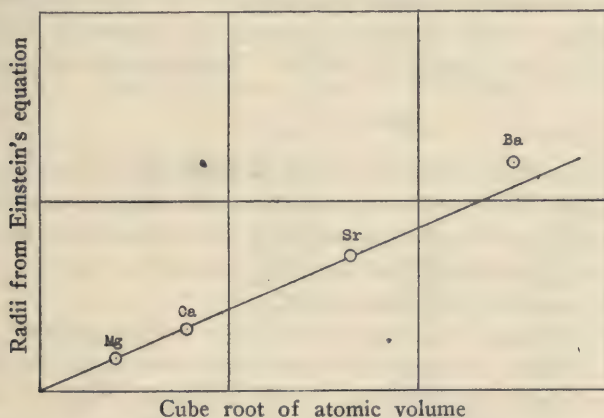


FIGURE 22. Relation of the Cube Root of Atomic Volume to Radii from Einstein's Equation.

authors of the Lorenz-Lorentz refraction formula that the ratio $(n^2 - 1)/(n^2 + 2)$ used in this formula represents the ratio of the true volume to the

²⁶ *Annalen der Physik*, 41, 524.

apparent volume of an atom. In both cases there is a linear relation between the atomic radii computed from our equation and the radii calculated by the other methods. This relation to the Heydweiller radii in two sets of spectral series from the alkali metals is shown in Figure 21, which is taken from page 204 of the article in *The Astrophysical Journal*, and a similar relation is shown between the radii calculated from our equation and the cube root of the atomic volume in the triplet series of spectra in magnesium, calcium and strontium in Figure 22, which is taken from page 207 of the same article.

It seems from the above that as far as we are able to gather data on atomic radii from other sources they tend to justify our assumption that radiating electrons are in revolution about a central charge, and hence to confirm our equation for calculating the magnitude of this charge.

ON THE ELEMENTARY CHARGE OF HYDROGEN

We have shown how it is possible to compute the central positive charge of a system consisting of an electron revolving about a positive nucleus from the wave-length of the radiation set up by the electron. We know, also, that in many radiating atomic systems there are series of lines whose wave-lengths may be computed by a mathematical formula from a single, hypothetical, convergence wave-length. This should make it possible to compute a charge, which we may call the convergence charge of the system, from the wave-length of any spectral line of a series.

The most successful formula yet proposed for computing the wave-lengths of a series of lines is the one proposed by Balmer in 1885²⁷ for a series of lines in the hydrogen spectrum. This formula as proposed by Balmer is

$$\lambda = h \frac{m^2}{m^2 - 4}$$

where h is the number $3645 \cdot 10^{-8}$ and m is given the successive integral values 3, 4, 5, etc. When m is taken as three the longest wave-length of the series is given, and for each succeeding value of m up to $m = 31$ the wave-length of a known hydrogen line is given with an accuracy as great as the possible accuracy of measurement.

It will be seen that as m becomes larger the fraction $m^2/(m^2 - 4)$ becomes more and more nearly equal to one, and the wave-lengths approach more and more nearly to the value of h , so that in the limit, $\lambda = h$, and h becomes the convergence wave-length of the system.

Our equation for the central charge acting upon a revolving electron is $Q = 2.882 \cdot 10^{-12}/\sqrt{\lambda}$. We may, if we choose, compute by this formula a central charge corresponding to every line in the Balmer series of hydrogen, and if our hypothesis is correct it should be possible to express

²⁷ *Wiedemann's Annalen*, 25, 80 (1885).

every one of these charges in terms of a fundamental charge by means of a formula similar to the Balmer wave-length formula.

Since in our equation the charge, Q , varies inversely as the square root of the wave-length, it will be more convenient to use the Balmer equation in the form in which it is generally written, viz., $1/\lambda = (m^2 - 4)/hm^2$. Then since Q varies as $1/\sqrt{\lambda}$, it should be possible to calculate Q from an equation of the form

$$Q = A\sqrt{\frac{m^2 - 4}{m^2}}$$

In this equation A becomes a fundamental atomic charge from which all the other charges may be calculated.

To find the value of A we then compute the value of Q for each spectral line of the series from the equation

$$Q = \frac{2.882 \cdot 10^{-12}}{\sqrt{\lambda}}$$

and divide this value of Q by

$$\sqrt{\frac{m^2 - 4}{m^2}}$$

using the value of m for the corresponding line. The results of this computation for the first nine lines of the Balmer series and for the line for which $m = 31$ are given in Table XXVII, which is taken from an article on "The Astronomical Atom and the Spectral Series of Hydrogen" in *The Astrophysical Journal* of July, 1918.

TABLE XXVII.
The Convergence Charge of the Balmer Series.

| m | $\lambda \cdot 10^8$ | $Q \cdot 10^{10}$ | $A \cdot 10^{10}$ |
|-----|----------------------|-------------------|-------------------|
| 3 | 6563.07 | 3.558 | 4.776 |
| 4 | 4861.57 | 4.135 | 4.774 |
| 5 | 4340.53 | 4.373 | 4.774 |
| 6 | 4102.00 | 4.496 | 4.769 |
| 7 | 3970.33 | 4.574 | 4.774 |
| 8 | 3889.15 | 4.618 | 4.771 |
| 9 | 3835.51 | 4.656 | 4.775 |
| 10 | 3798.00 | 4.678 | 4.774 |
| 11 | 3770.73 | 4.694 | 4.773 |
| 31 | 3661.31 | 4.763 | 4.773 |

The above values of A give a mean value of $4.773 \cdot 10^{-10}$ E. S. U. for the convergence charge of the hydrogen atomic system which gives rise

to the Balmer series. Since this is the magnitude of the unit electrical charge from the most careful measurements, we may write our equation for the effective charges for the various lines of the Balmer series,

$$Q = +e \sqrt{\frac{m^2 - 4}{m^2}}$$

where e is the unit electrical charge.

The Balmer formula is frequently written in the form,

$$1/\lambda = N(1/4 - 1/m^2).$$

The corresponding equation for Q then becomes

$$Q = A' \sqrt{1/4 - 1/m^2}.$$

If we compute A' from this equation it necessarily comes out twice as great as A in the preceding equation, and we may write

$$Q = +2e \sqrt{1/4 - 1/m^2}.$$

Since the value of Q increases with an increase of m until it becomes

$$Q = +2e \sqrt{1/4} = +e,$$

the convergence charge given by this equation is necessarily the same as by the other.

In 1896 Pickering²⁸ discovered in the spectrum of a very hot star another series of lines similar to the Balmer series for which he gave the formula

$$\lambda = 4650 \left(\frac{m^2}{m^2 - 4} \right) - 1032.$$

Later Ritz showed that the wave-lengths of this series could be calculated very exactly from the equation

$$1/\lambda = N \left(\frac{1}{4} - \frac{1}{(m + 0.5)^2} \right)$$

This equation leads to the same value of N as does the Balmer series, and as in the Balmer series, $Q = +2e \sqrt{1/4}$.

Since there has been doubt cast upon the origin of the Pickering series because Bohr's spectral theory will not permit the existence of such a series in hydrogen, it may be well to compute the convergence charge of the atomic system which gives this spectrum.

In Table XXVIII, which is taken from the paper quoted above, are given the values of $2e$ from the equation

$$2e = \frac{Q}{\sqrt{1/4 - 1/(m + 0.5)^2}}$$

as calculated from the first eight lines of the Pickering series. Q is computed, as before, from the equation $Q = 2.882 \cdot 10^{-12} / \sqrt{\lambda}$.

²⁸ *Astrophysical Journal*, 4, 369 (1896).

TABLE XXVIII.
The Convergence Charge of the Pickering Series.

| m | $\lambda \cdot 10^8$ | $Q \cdot 10^{10}$ | $2e \cdot 10^{10}$ |
|-----|----------------------|-------------------|--------------------|
| 3 | 5413.6 | 3.916 | 9.550 |
| 4 | 4542.4 | 4.276 | 9.545 |
| 5 | 4200.7 | 4.447 | 9.543 |
| 6 | 4026.0 | 4.542 | 9.542 |
| 7 | 3924.0 | 4.600 | 9.543 |
| 8 | 3860.8 | 4.641 | 9.549 |
| 9 | 3815.7 | 4.663 | 9.536 |
| 10 | 3783.4 | 4.686 | 9.544 |

The Pickering series accordingly gives for the convergence charges of its atomic system $+e = 4.772 \cdot 10^{-10}$ E. S. U.

Computations based on the electrochemical equivalent of hydrogen and the known number of molecules in one cubic centimeter of a gas lead to the conclusion that the charge on the hydrogen ion in electrolysis is equal in magnitude and opposite in sign to the charge of an electron. This hypothesis seems to be sustained, in so far as the evidence may apply, by the results of the preceding calculations. This does not exclude the possibility that the positive nucleus of a hydrogen atom may have a charge greater in magnitude than the unit electrical charge, and there are other lines in the hydrogen spectrum which indicate that this is actually the case.

Thus, there is a series of lines in the hydrogen spectrum which seems to correspond to the, so called, principal series of the alkali metals. All but one of the lines of this series lie in the ultra violet, and none of them has ever been observed in the vacuum tube discharge, but only in the very hot stars. Still, they are generally accepted as hydrogen lines.

The Ritz formula, from which the wave-lengths of the lines of this series may be calculated, is

$$1/\lambda = N[1/(1.5)^2 - 1/(m+1)^2],$$

where N has the same value as in the preceding equations. This equation transforms into

$$Q = +2e\sqrt{1/(1.5)^2 - 1/(m+1)^2}.$$

The values of $2e$ computed from this equation and a few of the lines of the series are given in Table XXIX.

The difficulties of measuring the wave-lengths of the lines of this series are greater than in the case of the two former series, and the individual values of $2e$ do not agree as closely as in the former cases, but the mean value, $2e = 9.554$, agrees perfectly with the former values.

TABLE XXIX.

Values of $2e$ From the Principal Series of Hydrogen.

| m | $\lambda \cdot 10^8$ | $Q \cdot 10^{10}$ | $2e \cdot 10^{10}$ |
|-----|----------------------|-------------------|--------------------|
| 1 | 4687.88 | 4.207 | 9.540 |
| 2 | 2734.55 | 5.510 | 9.551 |
| 3 | 2386.50 | 5.900 | 9.547 |
| 4 | 2253.74 | 6.067 | 9.540 |
| 5 | 2187.60 | 6.158 | 9.540 |

It is interesting to observe, however, that this series does not converge to a fundamental charge e , but to $Q = +2e\sqrt{1/(1.5)^2} = 6.366 \cdot 10^{-10}$ E. S. U. This indicates that there may be an atomic radiating system in hydrogen with a positive charge greater than $+e$. Since we know of no way of increasing a positive charge of an atom except by abstracting one or more electrons, and since the abstraction of an electron from an atom having a charge $+e$ should leave it with a charge $+2e$, it would seem possible to have a hydrogen atom with a nuclear charge $Q = +2e$. Such an atom should give off radiations of higher frequency than one with a charge $Q = +e$, and its spectrum should be looked for in the extreme ultra violet.

Ritz concluded from analogies in other spectra that there should be a series in hydrogen with the formula

$$1/\lambda = N \left(1 - \frac{1}{m^2} \right)$$

This is a simpler formula than the others and would accordingly seem to belong to a less complex atomic system.

In 1916 Lyman discovered three lines which seem to belong to the Ritz series. Their wave-lengths and the values of $2e$ calculated from the equation $Q = 2e\sqrt{1 - 1/m^2}$ are given in Table XXX. Since the wave-lengths cannot be measured with a high degree of accuracy in this part of the spectrum, the values of $2e$ computed from these lines do not agree as closely as in former cases. Two of the three, however, give values whose mean is in exact agreement with the former values of $+e$.

TABLE XXX.

Values of $2e$ from the Ritz-Lyman Series.

| m | $\lambda \cdot 10^8$ | $Q \cdot 10^{10}$ | $2e \cdot 10^{10}$ |
|-----|----------------------|-------------------|--------------------|
| 2 | 1216 | 8.258 | 9.302 |
| 3 | 1026 | 9.006 | 9.552 |
| 4 | 972 | 9.237 | 9.540 |

In this connection it should be noted that the best known value of the charge on an alpha-particle, which is apparently a helium atom minus

two electrons, indicates that this charge is $+2e$. The alpha-particle with a single electron should accordingly give a radiation with a convergence wave-length of 912. Since this is the convergence wave-length of the Ritz-Lyman series, this series might, so far as our evidence goes, belong to the helium atom as well as to hydrogen. As a matter of fact, Lyman is unable to say positively to which element it does belong, or whether it does not belong to both. Thus he says:²⁹ "In connection with Bohr's speculations it is important to observe that λ 1216, which forms the first member of the Ritz series, occupies exactly the same position when obtained from helium as when it is produced in hydrogen."

A possible argument in favor of the helium origin of this series may be found in the fact that our theory would give an orbital radius of $1.06 \cdot 10^{-8}$ to an electron having a central charge of $+2e$. The best determinations of the radius of the helium atom³⁰ give values of 1.09, 1.15 and .96. The mean of these values is 1.07, or within one per cent of our calculated value.

Lyman found no lines of wave-length less than 900 which could be attributed to hydrogen, though he found lines in the ultra violet with wave-lengths as short as $\lambda = 600$. It accordingly seems extremely probable that no hydrogen atomic system exists with a nuclear charge greater than $+2e$, but that there are other atomic systems with a greater charge than this.

The experimental evidence seems to point to the possibility of the existence of hydrogen in two atomic forms, in one of which the central positive charge is twice as great as in the other. This makes it worth while to inquire which is the normal condition of the hydrogen atom, or if one condition is more common than the other. As a matter of experience, hydrogen is never found in the form of neutral atoms, but the hydrogen atom is always found combined with another hydrogen atom or with some other atom or atoms. The hydrogen ion in electrolysis is known to be always positively electrified, and apparently with a charge $+e$. In the case of the luminous gas in a vacuum tube discharge it is still a question whether the luminous particles are charged ions or not. Sir J. J. Thomson and Knipp, in the case of the experiments already mentioned, seem to have found hydrogen atoms with a charge of approximately $+e$ in their tubes, but in no case to have found what they regarded as negatively electrified hydrogen ions, nor hydrogen ions with a charge of $+2e$.

On the other hand, Strutt found in his investigation on "Duration of Luminosity of Electric Discharge in Gases and Vapours"³¹ that the

²⁹ *Astrophysical Journal*, 43, 100 (1916).

³⁰ "Kaye and Laby's Tables," p. 33.

³¹ *Royal Society Proceedings*, 94, 88 (1917).

luminous hydrogen atoms which gave the Balmer series were universally electronegative, and that when deflected to one side of the field they showed no traces of any other lines than those of the Balmer series. If the normal charge of the hydrogen atom is $+2e$ it would have to annex an electron in order to reduce its charge to $+e$, as it seems to be in the Balmer and Pickering series. If, on the other hand, its normal charge is $+e$, its charge $+2e$ could only be given by abstracting an electron, and the principal series and the Ritz-Lyman series would be given by positively charged ions.

The above argument does not undertake to explain the mechanism of radiation nor to account for the various lines in a spectrum so relatively simple as that of hydrogen. What it does undertake is to show that the wave-lengths of all the lines in the known hydrogen series may be computed by simple formulae which involve as a constant one of the best known physical quantities, namely, the unit electrical charge. Thus the wave-lengths of the lines of the Balmer series may be calculated from the equation

$$\lambda = \frac{8.306 \cdot 10^{-24}}{e^2 \left(\frac{m^2 - 4}{m^2} \right)}$$

It also undertakes to give a physical significance to the Rydberg frequency constant, N , which has been used in the above computations. Rydberg has proposed as a general formula for computing the wave-lengths of spectral series the equation

$$1/\lambda = A + \frac{N}{(m + \mu)^2}$$

where N is regarded as a universal constant and A and μ are constants to be determined for each series. In this equation A becomes the reciprocal of the convergence wave-length and N a reciprocal wave-length which is modified for each spectral line. While this formula does not apply as widely as its author hoped it would, the constant N has been adopted in nearly all the series formulae since proposed, and it is quite generally believed to be a universal constant. We have shown in the above discussion that N is the reciprocal wave-length of an electron revolving about a charge $Q = +2e$, that is, the charge of an alpha-particle and perhaps of the hydrogen nucleus. Since the alpha-particle seems to play so large a part in the construction of atoms of all kinds, it is not surprising that its charge should appear as an important factor in calculating radiation frequencies of the different spectra.

Hitherto all spectral formulae have been purely empirical. With the exception of some proposed by Ritz none of them has any theoretical basis, and Ritz based his formulae upon an atomic model which no one supposes conforms in any way to reality. The Bohr hypothesis, which

has attracted considerable attention, frankly gives up the explanation of radiation and assumes it to be governed by some undiscovered system of mechanics while it assumes its hypothetical atom while not radiating to violate the best known laws of electromechanics.

Konen,⁸² in referring to the purely empirical character of spectral formulae, says that no relation between any of the constants used in these computations and any physical properties of the atom have ever been discovered. He admits as the one possible exception to this statement the relation between the ionic charges of certain elements and the convergence frequencies of their corresponding spectral series, to which attention was called by the present writer in the *Astrophysical Journal* of October 1912, but he ends by rejecting the ionic charges as true physical constants.

This objection can scarcely hold to the unit electrical charge, which it is here shown may be calculated from the wave-lengths of the lines of the several series of hydrogen with as high a degree of accuracy as from any known data. It will later be shown that the same may be said of the X-ray spectra.*

POSITIVE ATOMIC CHARGES AND X-RAYS

It was eighteen years after the discovery of X-rays by Roentgen that they were proved to be wave-trains similar to those of light, but of much shorter wave-length. In 1912 Laue conceived the idea of using the supposed orderly arrangement of atoms in a crystal as a means of producing regular diffraction patterns with X-rays, and his suggestions were successfully carried out by Friedrich and Knipping in 1913. Soon after Laue's discovery the Braggs showed that X-rays may also be regularly reflected from the cleavage planes of crystals, and that by using the reflection from a large number of successive planes the wave-length of X-rays may be measured in terms of the distance between the reflecting crystal planes.

By making use of the Bragg method Moseley was able in 1914 to measure the wave-length of certain strong lines in the X-ray spectra of a considerable number of elements. Siegbahn and others have extended Moseley's measurements to include the elements from sodium to uranium, so that the X-ray spectra of all but a few of the elements of lowest atomic weight are known with a close degree of approximation.

⁸² "Das Leuchten der Gase und Dämpfe," p. 195.

*Since this paper has been put in type the writer has succeeded in calculating the unit electrical charge from each of the six series in helium with nearly the same degree of accuracy as from the Balmer series and by means of formulae but slightly modified from the Balmer formula. See *Astrophysical Journal*, June, 1919.

In his second and last paper on "High Frequency Spectra"⁸³ Moseley says:

The frequency of any line in the X-ray spectrum is approximately proportional to $A(N-b)^2$, where A and b are constants and where N is the atomic number.

Moseley found the spectral bands which had been named the K - and L -radiation in many of these elements, and for the strongest line of the K -radiation he found b in the above equation to equal 1 and for the strongest line of the L -radiation he found $b = 7.4$.

Moseley surmised that the significance of the serial atomic number N in the above equation might be explained on Van den Broek's hypothesis that N represents the number of units of positive electricity in the atomic nucleus. He did not show what this unit of positive electricity is, nor how the nuclear charge may be computed.

In a paper in the *Physical Review* of May, 1917, the present writer showed that on the assumption of an orbital motion of the radiating electrons the nuclear charge may be computed from the equation which has already been used in this paper for computing the hydrogen charge. Instead of using the most exact values of e and m in the calculation made at that time, only approximate values were used, and the computation of Q , the nuclear charge, was made with a small slide rule, as the measurements of the wave-lengths did not seem to justify more accurate computations. As a result, the equation

$$Q = \frac{2.95 \cdot 10^{-12}}{\sqrt{\lambda}}$$

was used instead of the more accurate formula

$$Q = \frac{2.882 \cdot 10^{-12}}{\sqrt{\lambda}}$$

Moseley's equations showed that ν , the frequency of the X-rays, varied as $(N-b)^2$, but since the atomic charge varies as the square root of the frequency, Moseley's equation should transform into $Q = A'(N-1)$ for the K -radiation and $Q = A'(N-7.4)$ for the L -radiation. When this expression for the K -radiation was equated with that for the atomic charge, thus

$$A'(N-1) = \frac{2.95 \cdot 10^{-12}}{\sqrt{\lambda}}$$

it was found that $A' = 2e$, approximately as shown in Table XXXI. Table XXXI as here given is taken from the writer's former paper, and it is seen that both equations give the same value for the nuclear charges of the atoms, but that wave-lengths $\lambda\beta$, which are shorter than $\lambda\alpha$, gave a charge approximating more closely to $2e$ than the charge computed from $\lambda\alpha$. The inference was drawn that if the shortest wave-length of the K -radiation could be known, it would give a nuclear charge of exactly $2e(N-1)$.

⁸³ *Philosophical Magazine*, 27, 703 (1914).

TABLE XXXI.
Nuclear Charges from K-radiation.

| Atom | No. | $\lambda\text{-}\alpha$ | $Q\text{-}\alpha$ | | $\lambda\text{-}\beta$ | $Q\text{-}\beta$ | |
|------|-----|-------------------------|--|---------------------|------------------------|--|--------------------|
| | | | $\frac{2.95 \cdot 10^{-12}}{\sqrt{\lambda}}$ | $8.51(N-1)10^{-10}$ | | $\frac{2.95 \cdot 10^{-12}}{\sqrt{\lambda}}$ | $8.9(N-1)10^{-10}$ |
| | | | | | | | |
| Na | 11 | 11.951 | 85.3 | 85.1 | | | |
| Mg | 12 | 9.915 | 93.7 | 93.6 | 9.477 | 96.5 | 97.9 |
| Al | 13 | 8.362 | 102 | 102 | 7.954 | 104.7 | 107 |
| Si | 14 | 7.136 | 110.3 | 110.6 | 6.744 | 113.6 | 115.7 |
| P | 15 | 6.168 | 119 | 119.2 | 5.808 | 122.5 | 124.7 |
| S | 16 | 5.360 | 127 | 127.6 | 5.018 | 132 | 133.5 |
| Cl | 17 | 4.730 | 135.6 | 136.1 | 4.394 | 140.5 | 142.4 |
| K | 19 | 3.747 | 155 | 153.3 | 3.456 | 159 | 160 |
| Ca | 20 | 3.363 | 160.6 | 161.5 | 3.090 | 167.5 | 169 |
| Se | 21 | 3.030 | 169 | 170 | 2.778 | 176.5 | 178 |
| Ti | 22 | 2.751 | 178 | 178.6 | 2.516 | 186 | 187 |
| V | 23 | 2.509 | 187 | 187 | 2.294 | 194.5 | 196 |
| Cr | 24 | 2.293 | 194.5 | 195.7 | 2.086 | 204 | 204.6 |
| Mn | 25 | 2.103 | 203 | 204 | 1.860 | 216 | 214 |
| Fe | 26 | 1.938 | 212 | 212.4 | 1.756 | 223 | 222.5 |
| Co | 27 | 1.798 | 220 | 221.6 | 1.629 | 230.3 | 231.5 |
| Ni | 28 | 1.662 | 228.4 | 229.8 | 1.506 | 239.7 | 240 |
| Cu | 29 | 1.549 | 238 | 238 | 1.402 | 250 | 249 |
| Zn | 30 | 1.445 | 244 | 246.6 | 1.306 | 258.5 | 258 |
| Y | 39 | 0.841 | 322 | 323 | 0.757 | 339 | 338 |
| Zr | 40 | 0.800 | 330 | 332 | 0.718 | 348.5 | 347 |
| Nb | 41 | 0.750 | 340.6 | 340.5 | | | |
| Mo | 42 | 0.716 | 349 | 349 | 0.631 | 372 | 367 |
| Ru | 44 | 0.641 | 368.5 | 366 | 0.569 | 392 | 383 |
| Pd | 46 | 0.587 | 387.5 | 383 | 0.522 | 408 | 400 |
| Ag | 47 | 0.562 | 393.5 | 392 | 0.499 | 418 | 410 |
| Cd | 48 | 0.535 | 403 | 400 | 0.471 | 430 | 418 |
| In | 49 | 0.511 | 412.5 | 409 | 0.448 | 441 | 427 |
| Sn | 50 | 0.485 | 424 | 417 | 0.427 | 452 | 436 |
| Sb | 51 | 0.449 | 441 | 426 | 0.396 | 468 | 445 |
| Ba | 56 | 0.383 | 476 | 468 | 0.334 | 511 | 490 |
| La | 57 | 0.373 | 483 | 477 | 0.326 | 517 | 498 |

In the *Physical Review* of December, 1917, Blake and Duane published a paper on "High Frequency X-Rays," in which are given the wave-lengths of the K-radiation absorption band for twenty-one elements. These wave-lengths are considerably shorter than the emission wave-lengths of the same lines. The authors explain this on the ground that in the case of reflection from a crystal face a correction for the distance of penetration into the crystal before reflection should be made, while in the case of the absorption spectrum this correction does not appear. This penetration tends to make the reflected wave-length appear longer than the actual wave-length.

The authors find that the frequency of the absorbed radiation may be calculated very exactly from Moseley's equation, using the value 3.5, instead of 1, for b , and that in this case A of Moseley's equation becomes the Rydberg frequency, 109675 multiplied by the velocity of light. They say:

As is well known, equations can be written out containing Rydberg's fundamental frequency as a coefficient, that approximately represent the frequencies of the characteristic lines of the elements as functions of the atomic numbers. It is interesting to note (see next-to-last column of the table) that the equation

$$\nu = \nu_0 (N - 3.5)^2$$

in which ν_0 is the Rydberg fundamental frequency (namely, 109,675 multiplied by the velocity of light), represents with considerable accuracy our experimental results. In this equation N stands for the atomic number of the element, and the only constant determined by the X-ray experiments is that in parentheses, namely, 3.5. It is interesting, too, to note that this equation gives us the correct value of the nuclear charge as worked out by Sanford from the assumption of equality between orbital and vibration frequencies. For we have

$$\nu = \frac{2 \pi^2 e^4 m}{h^3} (N - 3.5)^2$$

and Q , the nuclear charge, fulfills the equation

$$Q^2 = \frac{v^2 h^2}{\pi^2 e^2} = \frac{2 h^3 \nu}{\pi^2 e^2 m}$$

Eliminating ν , we get at once $Q = 2e(N - 3.5)$, an equation that manifestly holds to the accuracy shown in the table for the elements there shown. Thus it would appear that a knowledge of the position of the X-ray absorption lines, which corresponds to the head of the emission line series, leads to results that are more fundamental than a knowledge of the position of the principal emission lines can.

These measurements of Blake and Duane accordingly establish beyond a doubt that the convergence wave-lengths of the K -radiation series may be computed by a formula using only the factors $2e$ and the atomic number with numerical constants, thus

$$\lambda = \left(\frac{2.882 \cdot 10^{-12}}{2e(N - 3.5)} \right)^2$$

The K -radiation has been observed in no element of lower atomic number than eleven, and it would seem from this equation that no element having an atomic number less than four could give off K -radiation. Even in the case of Beryllium, whose atomic number is four, the central atomic charge would be $Q = 2e(4 - 3.5) = e$, and the wave-length of its K -radiation would be $\lambda = 3645 \cdot 10^{-8}$, which is the convergence wave-length of the Balmer and Pickering series in hydrogen.

While no X-ray wave-lengths shorter than those of sodium have been measured, Barkla and White⁸⁴ conclude from their measurements of the absorption of X-rays in carbon, oxygen and aluminium that these elements are capable of giving off a radiation of still higher frequency than the

⁸⁴ *Philosophical Magazine*, 34, 275 (1917).

K-radiation. Such a radiation had formerly been suggested by Barkla and called the *J*-radiation. The estimated wave-lengths for this radiation are as follows:

$$\text{Carbon} \quad \lambda = .42 \cdot 10^{-8}$$

$$\text{Oxygen} \quad \lambda = .39 \cdot 10^{-8}$$

$$\text{Aluminium} \quad \lambda = .37 \cdot 10^{-8}$$

Such wave-lengths require nuclear charges of about $100e$. Thus, for carbon, $Q = 444 \cdot 10^{-10}$ E. S. U. Such a nuclear charge seems very improbable. It is also true that if Moseley's equation be applied to Barkla and White's wave-lengths it gives values of b , which are all negative, and which are wholly inconsistent with each other.

It was shown in the writer's earlier paper that when the nuclear charges for the *L*-radiation were computed, using Moseley's value of b , the unit charge, e , did not appear in the equation, but it was shown that when the nuclear charges for the two bands of radiation were computed by our formula for the same element they differed in every case by an integral number of unit electrical charges, namely, by $e(N + 5)$, where N is the atomic number of the element. This is shown in Table XXXII, which is taken from the earlier paper, and which includes all the elements for which the wave-lengths of both the *K*- and *L*-radiation were then known.

TABLE XXXII.
Difference in K- and L-radiation Charges.

| Atom | No. | Q_K | Q_L | $Q_K - Q_L$ | $\frac{Q_K - Q_L}{(N+5)}$ |
|------|-----|-------|-------|-------------|---------------------------|
| Zr | 40 | 332 | 118 | 214 | 4.76 |
| Nb | 41 | 340.5 | 122.7 | 217.8 | 4.74 |
| Mo | 42 | 349 | 126.3 | 222.7 | 4.74 |
| Ru | 44 | 366 | 133.6 | 232.4 | 4.74 |
| Pd | 46 | 383 | 141 | 242 | 4.75 |
| Ag | 47 | 392 | 144.6 | 247.4 | 4.76 |
| Sn | 50 | 417 | 155.2 | 261.8 | 4.76 |
| Sb | 51 | 426 | 159 | 267 | 4.77 |
| La | 57 | 477 | 181 | 296 | 4.77 |

Since the publication of the paper referred to, Friman³⁵ has given the wave-lengths of a large number of lines in the *L*-radiation series of thirty-four elements, giving wave-lengths in some cases for as many as twelve lines in the *L*-spectrum of a single element. The arrangement of these lines is similar to that in the visible band spectra of some of the elements. The lines are closer together as their wave-lengths grow less, and while no series formula is known for them, they suggest that in each

³⁵ *Philosophical Magazine* 32, 497 (Nov., 1916).

element there is a convergence wave-length, just as there is in the hydrogen series. If the analogy with visible radiation is real, these convergence wave-lengths should be used in computing the nuclear charge of the radiating system. Since we cannot know the convergence wave-lengths we can do no better than compute the nuclear charge for the shortest corresponding wave-lengths given.

Friman has arranged his data to show which he regards as corresponding lines in the spectra of the different elements, but in several cases he has given wave-lengths for only from one to four lines in a spectrum, and these are the lines with the greatest wave-length. He has given for eleven elements the wave-lengths of a line which he calls γ_8 , which is next to the shortest wave-length measured, the shortest being given for only two elements.

When the wave-lengths of Friman's γ_8 lines are used it is found that their nuclear charges may be computed with as high a degree of accuracy as the wave-lengths are known by the formula $Q = e(N - 15.4)$.

This fact may be shown in another way by computing the wave-lengths from this formula and our other formula for the nuclear charge. Thus, from our formula for orbital motion:

$$\sqrt{\lambda} = \frac{2.882 \cdot 10^{-12}}{Q}$$

If Q be computed from the atomic number it becomes $Q = e(N - 15.4)$. Substituting this value of Q in the equation for λ , we have

$$\lambda = \left(\frac{2.882 \cdot 10^{-12}}{e(N - 15.4)} \right)^2$$

The two values of λ as measured by Friman and as calculated from the above formula are given in Table XXXIII, which includes all the elements for which Friman has given the wave-lengths of the γ_8 line.

TABLE XXXIII.
Wave-Lengths of $L\text{-}\gamma_8$ Lines.

| Element | N | $\lambda \cdot 10^8$ meas. | $\lambda \cdot 10^8$ cal. | Dif. |
|---------|-----|----------------------------|---------------------------|-------|
| Sn | 50 | 2.889 | 3.040 | +151 |
| Pr | 59 | 1.933 | 1.920 | -.013 |
| Nd | 60 | 1.775 | 1.830 | +.055 |
| Eu | 63 | 1.590 | 1.582 | -.008 |
| Gd | 64 | 1.558 | 1.548 | -.010 |
| Tb | 65 | 1.470 | 1.480 | +.010 |
| Dy | 66 | 1.418 | 1.414 | -.004 |
| Ho | 67 | 1.365 | 1.370 | +.005 |
| Er | 68 | 1.316 | 1.316 | |
| Yb | 70 | 1.223 | 1.223 | |
| Lu | 71 | 1.183 | 1.184 | +.001 |

This computation gives the wave-lengths with an accuracy as great as the accuracy of measurement in the case of all except tin. Friman gives another wave-length measurement for this element for which $\lambda = 2.999$, a difference of .04 from the wave-length calculated by our formula. Moseley's and Friman's measurements of the strongest lines in the L -radiation regularly differed in the second decimal place, and these lines are more easily measured than the γ_s lines.

In two elements Friman found single lines with wave-length less than that of the γ_s lines. These lines give somewhat smaller values for b , and it seems not improbable that the L -series converges to a wave-length for which $b = 15$.

In the *Physical Review* of June, 1918, E. Dershem gives the wave-lengths of nineteen lines in the L -radiation spectrum of tungsten. His list includes two lines of shorter wave-length than would be given by the above formula. Only one of these lines has been observed by any previous investigator. The formula would give for tungsten, for which $N = 74$,

$$\lambda = \left(\frac{2.882 \cdot 10^{-12}}{58.6e} \right)^2 = 1.061.$$

A double line of this wave-length has been observed by nearly all investigators of the tungsten spectrum. Siegbahn and Friman⁸⁶ give the wave-lengths of these lines as 1.058 and 1.064. Ledoux-Lebard and Dauvillier⁸⁷ give their wave-lengths as 1.062 and 1.067. Dershem gives them 1.058 and 1.064. It would accordingly seem that our formula for the wave-length of the L -radiation still applies to an element of atomic number as great as 74.

It seems to be definitely shown from the above that the wave-lengths of the shortest lines in the L -radiation series, as in the K -radiation, may be accurately calculated by a formula involving the unit electrical quantity as a constant, and with the serial atomic number as the only variable quantity. We find here, also, the same phenomenon as in the different series of the visible spectrum of hydrogen; i.e., the lines of the L -series, like the Balmer and Pickering series of hydrogen, may have their convergence wave-lengths calculated from a formula involving a single unit electrical charge, while the K -radiation formula, like the formulae of the principal series and the Ritz-Lyman series of hydrogen, involves the use of the factor $2e$.

In the case of the nuclear charges, we find that the atomic systems which give the K -radiation have their charges increased by $2e$ in passing from one element to the next higher in the series, while the atoms which

⁸⁶ *Philosophical Magazine*, July, 1916.

⁸⁷ *Comptes Rendus*, April 30, 1917.

give the L -radiation have their charges increased by only one unit charge under the same circumstances.

ORBITAL VELOCITY OF ELECTRONS WHICH PRODUCE X-RAYS

If the formula for the nuclear charge in K -radiation applies to uranium, for which $N=92$, $Q=2e(92-3.5)=945\cdot10^{-10}$ E. S. U. Since from our fundamental equations $v\sqrt{\lambda}=6.60\cdot10^8$ while $Q\sqrt{\lambda}=2.882\cdot10^{-12}$, $v/Q=2.29\cdot10^{17}$, nearly, and $v=1.94\cdot10^{10}$ cm/sec. for the K -radiation electrons of uranium. This would be the highest orbital speed reached by any electron giving off K -radiation, and is about 0.647 the velocity of light.

Much higher speeds than this are apparently reached by the electrons expelled from radioactive substances. Kaufmann used speeds which he believed to be more than 0.9 the velocity of light, and while his determinations were liable to large inaccuracies, other observers have measured speeds more than 0.9 the velocity of light.

A speed of even 0.8 the velocity of light, if due to orbital revolution in a system to which the photoelectric equation, $\frac{1}{2}mv^2=h\nu$, applies, would require a nuclear charge of about $1050\cdot10^{-10}$ E. S. U.; a charge ten per cent greater than would be given by the K -radiation formula for uranium.

The wave-lengths of the γ -radiation which accompanies the expulsion of high speed electrons from radioactive substances have been measured in a few cases. Rutherford and Andrade⁸⁸ give wave-lengths of fourteen lines from the γ -ray spectra of $Ra-B$ and $Ra-C$. Five of these lines with wave-lengths from $0.99\cdot10^{-9}$ to $1.69\cdot10^{-9}$ comprise a group which the authors believe belongs mainly to $Ra-C$, though they are unable to separate the two spectra.

In a later paper by Rutherford on "The Connexion between β and γ Ray Spectra,"⁸⁹ are given tables of the speeds of β -particles projected from $Ra-B$ and $Ra-C$, and it is interesting to compare these speeds with the orbital speeds which correspond to the wave-lengths of the accompanying γ -radiation.

In Table XXXIV the measured velocity of electrons expelled from $Ra-B$ are given in the first column, the velocity of electrons from $Ra-C$ in the second column, the observed wave-lengths of the γ -ray spectra of $Ra-B$ and $Ra-C$ in the third column, and in the fourth column are the orbital speeds of the electrons which should give the wave-lengths in the third column. The velocities in the first and fourth columns which seem to agree are preceded by the same letters.

⁸⁸ *Philosophical Magazine*, 28, 270 (1914).

⁸⁹ *Philosophical Magazine*, 28, 305 (1914).

It will be seen that all the speeds but one that are given in the second column are higher than the computed speeds from the wave-lengths of the spectral lines, but that there is a close agreement between five of the computed speeds in the fourth column and measured speeds of electrons from *Ra-B*, and that the orbital speeds corresponding to the shortest and longest wave-lengths agree exactly with the measured speeds of the fastest and slowest electrons expelled from *Ra-B*.

TABLE XXXIV.

Comparison of the Speeds of β -Rays with the Orbital Speeds of Electrons in γ -Radiation.

| Velocity of β -Rays | | Wave-Lengths <i>Ra-B</i> & <i>Ra-C</i> | Orbital v. |
|---------------------------|-----------------------|---|------------------------|
| <i>Ra-B</i> | <i>Ra-C</i> | | |
| A $2.469 \cdot 10^{10}$ | $2.926 \cdot 10^{10}$ | $0.71 \cdot 10^{-9}$ | A $2.47 \cdot 10^{10}$ |
| 2.45 | 2.917 | 0.99 | B 2.095 |
| 2.391 | 2.906 | 1.15 | C 1.94 |
| 2.361 | 2.892 | 1.37 | 1.735 |
| 2.286 | 2.877 | 1.59 | 1.625 |
| 2.252 | 2.856 | 1.69 | 1.605 |
| 2.193 | 2.838 | 1.96 | 1.49 |
| 2.157 | 2.751 | 2.29 | 1.38 |
| B 2.10 | 2.604 | 2.42 | 1.34 |
| 1.968 | 2.250 | 2.62 | D 1.29 |
| C 1.905 | | 2.96 | 1.213 |
| D 1.278 | | 3.24 | 1.16 |
| 1.242 | | 3.93 | 1.05 |
| E 1.015 | | 4.28 | E 1.01 |

Rutherford and Andrade give reasons for believing that the lines of wave-length 1.37, 1.59 and 1.69 are from *Ra-C*. Since *Ra-C* is regarded as an isotope of bismuth with atomic number 83, its characteristic *K*-radiation should, from our formula, have a wave-length of $1.44 \cdot 10^{-9}$, which would bring it within this group. *Ra-B*, with an atomic number 82, should also have its characteristic *K*-radiation within this group, viz., at $\lambda = 1.47 \cdot 10^{-9}$.

It seems that, on the whole, the evidence is not unfavorable to the hypothesis that the β -particles projected from radioactive elements derive their high speeds from orbital revolution within their atoms.

Rutherford and Andrade conclude that the "soft" rays emitted by *Ra-B* belong to the *L* series of that element and that the strong pair of lines in the table at 1.59 and 1.69 represent the *K* series of both *Ra-B* and *Ra-C*.

Since *Ra-C* gives a penetrating radiation of only half the wavelength of its *K*-radiation line, Rutherford and Andrade conclude that:

In the case of radium C, and probably also thorium B, which emits an even more penetrating radiation than radium C, another type of characteristic radiation is emitted which is of higher mean frequency than for the "K" series. In other words, it is possible, at any rate in heavy elements, to obtain a line spectrum which is of still higher frequency than the "K" type. This may for convenience be named the "H" series, for no doubt evidence of a similar radiation will be found in other elements when bombarded by high speed cathode rays.

If we compare the "H"-radiation proposed by Rutherford and Andrade with the *J*-radiation proposed by Barkla, we find that in the case of the latter, if we accept the wave-lengths proposed by Barkla and White for carbon, oxygen and aluminium, an element of higher atomic number than about 35 would have its *J*-radiation electrons revolving at a speed higher than the velocity of light, and hence the *J*-radiation would be impossible in any of the principal radioactive elements.

Relation of the Nuclear Charge in Radiation to the Ionic Charges in Electrolysis

We have shown that characteristic atomic charges may be calculated from visible radiation (in the case of the hydrogen spectrum), from both the *K*- and *L*-radiations and from the γ -radiation of radium-*B*. We have also shown that the unit electrical charge is in all cases one of the factors in this computation and that the only variable quantity in any of the equations is the atomic number.

It has also been shown that characteristic charges, which seem to be the most important factor in all cohesion phenomena, may be approximately calculated from the mobility of electrolytic ions, and it has been shown in Table XXIV and in Figure 16 that these charges also bear a definite relation to the atomic numbers.

In order that the relation between these ionic charges and the nuclear charges in radiation may be seen more clearly, it remains to show that the former, like the latter, may be calculated by means of an equation of the form of Moseley's equation, and, finally, that either kind of charge may be calculated from the other by an equation of this same simple form.

The ionic charges which have heretofore been used in this discussion were based upon the hydrogen charge taken as five units, but we have called attention to the fact that the best data derived from electrolysis seem to show that each positive hydrogen ion carries a charge of $4.77 \cdot 10^{-10}$ E. S. U. In order to compare our ionic charges with our nuclear charges it becomes necessary to reduce them to electrostatic units on this basis. This is done and the results are shown in the third column

of Table XXXV, while in the fourth column are given the charges calculated from the equation $Q = 2.6(N - 4)$ for the same elements. All the monovalent elements whose ionic mobilities are known are given in the table.

TABLE XXXV.

Charges of Electrolytic Ions Calculated from Ionic Mobilities and from Atomic Numbers.

| Element | N | Ionic Chg. | $Q=2.6(N-4)$ |
|---------|-----|------------|--------------|
| Li | 3 | 2.8 | 2.6 (?) |
| F | 9 | 14 | 13 |
| Na | 11 | 15.05 | 18.2 |
| Cl | 17 | 34.8 | 33.8 |
| K | 19 | 37.8 | 39 |
| Br | 35 | 81.2 | 80.6 |
| Rb | 37 | 87 | 85.8 |
| I | 53 | 126.5 | 127.4 |
| Cs | 55 | 135.4 | 132.6 |
| Tl | 81 | 203 | 200.2 |

It will be seen from Table XXXV that with the single exception of sodium the ionic charges calculated by the two methods agree more closely than do the determinations of mobility by the most careful experimenters, and it seems highly probable that the values calculated from the atomic number equation are the better values.

It does not follow that the equation used is the one which expresses the true values most accurately, as it is possible to modify the equation without greatly affecting the values of the computed charges. Thus, $Q = 2.7(N - 5)$ gives quantities which agree with the charges calculated from ionic mobilities almost as well as do the charges given in Table XXXV.

It will be observed that in the case of our equation for ionic charges the factor e does not appear and hence these charges do not increase by integral multiples of the unit charge in passing from one ion to the one of next higher atomic number, but by a smaller quantity, viz., $2.6 \cdot 10^{-10}$ E. S. U. This is very close to the charge of the lithium ion as determined by its mobility, but the significance of this fact, if it has significance, does not appear.

Since both the ionic charges and the nuclear charges may be computed from the atomic numbers by the use of similar equations, it follows that one set of these charges may be computed from the other set. This is shown in Table XXXVI, in which Q_e represents the charge of the electrolytic ion and Q_k the nuclear charge in the K -radiation.

TABLE XXXVI.

Ionic Charges Calculated from Nuclear Charges.

| Element | Q_n | $\frac{(Q_k - e)}{3.68}$ |
|---------|-------|--------------------------|
| F | 13 | 13.4 |
| Na | 18.2 | 17.9 |
| Cl | 33.8 | 33.8 |
| K | 39 | 38.9 |
| Br | 80.6 | 80.6 |
| Rb | 85.8 | 85.7 |
| I | 127.4 | 127.3 |
| Cs | 132.6 | 132.5 |
| Tl | 200.2 | 200 |

In the case of multivalent ions the charges computed from the mobility are not so readily calculated from the nuclear charges, though within groups of similar elements the relation is still very striking. It is not to be doubted that the mobility of multivalent ions is, in general, less accurately known than that of monovalent ions.

In the case of Mg, Ca, Sr and Ba the ionic charges may be calculated from the nuclear charges in *K*-radiation very accurately except in the case of Ba. This relation is shown in Figure 23. In this figure, the *K*-radiation nuclear charges are shown as abscissas and the ionic charges as ordinates.

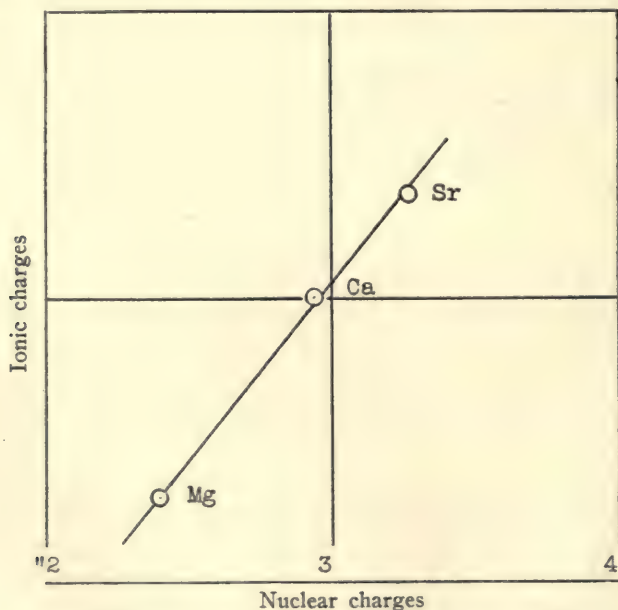


FIGURE 23. Relation of the Nuclear Charges Calculated from *K*-Radiation to Ionic Charges.

In Figure 24 the same relation is shown between the charges of ions from hot metals as computed from Richardson and Hulbirt's data and the charges of the same elements as calculated for their *L*-radiation nuclei. This figure should be compared with Figure 20.

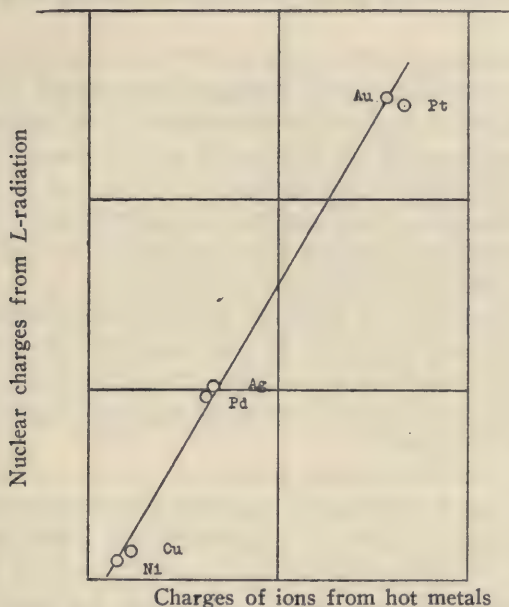


FIGURE 24.—Relation of Nuclear Charges in *L*-Radiation to Charges of Ions from Hot Metals.

The above relations seem to show beyond a doubt that the characteristic charges of the ions in electrolysis are largely determined by the nuclear charges of the atoms from which they are derived.

CHARACTERISTIC CHARGES OF METALS IN THE SOLID STATE

In our discussion up to this point we have dealt with the characteristic charges of the elements as electrolytic ions in water solution and as gaseous atoms and ions; but we have shown that these charges play a fundamental part in cohesion, and hence that the physical properties of the elements in both the liquid and solid states of aggregation must be determined largely by the characteristic charges of their atoms. Indeed, it has already been shown that the cohesion series and the contact electromotive series of the metals run parallel to each other, and that cohesion in solids, as in gases, is greater between electronegative than between electropositive atoms. It still remains to show that the characteristic charges which appear in electrolytic and gaseous ions may be detected in the solid state of aggregation.

This has already been attempted by the writer in a paper presented to a joint meeting of Section B of the American Association for the Advancement of Science and the American Physical Society, at Berkeley, California, August 5, 1915, and published in *Science* of March 24, 1916. The discussion here given follows similar lines to those laid down in the above-mentioned paper.

At the beginning of this paper attention was called to Bennett's discovery of the opposite electrification of two metals by their mere contact with each other, and to his conclusion that different metals have different adhesive forces for the electrical fluid. Bennett also applied the same notion to non-metallic substances, as Franklin had already done before him. Thus Bennett explains the electrification of the glass cylinder of his electrical machine when rubbed by silk by the greater adhesion of electricity for glass than for silk.

Cavallo, as a result of an extensive series of experiments, also came to the conclusion that "Different bodies have different capacities for holding the electric fluid," and Volta believed that the electric current was due in some way to the greater attraction of electricity by one of the metal plates than by the other.

Meanwhile, Fabroni had called attention to the change in oxidizability of a metal which may be induced by mere contact with another metal, and he had given his opinion that this change indicates a change in cohesion in the metal. He did not attribute this change in cohesion to the transference of electricity from one metal to the other, but this interpretation of the phenomenon was later proposed by Berthollet, as may be gathered from a translation in *Nicholson's Journal*⁴⁰ of a part of Berthollet's "Essai de Statique Chimique."

After a discussion of a number of experiments performed by Charles and Gay Lussac for the purpose of deciding whether the dissipation of a fine wire by the electric discharge of a Leyden jar was due to the heating effect of the spark or to some other cause, and their conclusion that the wire was not vaporized by heat, Berthollet concludes that the dispersion of the metallic particles precedes their oxidation, and says:

Electricity favors this oxidation, inasmuch as it diminishes the force of cohesion; it is thus that an alkali renders the action of sulphur on oxygen much more powerful, by destroying the force of cohesion opposed to it, and that a metal dissolved in an amalgam is oxidized more easily than when it is in the solid state.

All the chemical effects produced in substances submitted to the action of electricity seem capable of being deduced from these considerations, and of being explained by the diminution of the force of cohesion, which is the obstacle to the combinations which their molecules tend to form; but the differences which may be offered by positive electricity and negative electricity remain to be determined.

⁴⁰ *Nicholson's Journal*, 8, 80.

The fundamental question at issue seems to be, Are the charges which are found upon two plates of different metals when they have been placed in contact and then separated due to some chemical action which has taken place at the time of contact, or were the two metals before they were brought into contact already electrically different with respect to each other?

It has quite commonly been held that two metals which have been discharged to earth or to the inside of a hollow conductor are in absolutely the same electrical state, i.e., that they are in a condition of absolute electrical neutrality. Others have believed that the change in the electrical state of both metals when they are brought into contact with each other proves that they were not electrically neutral to each other before contact.

Among the physicists who have maintained that the electrical rearrangement which takes place at the time of contact of two metals is due to the different chemical action of the surrounding medium upon the two metals, no one has taken a more prominent part on the theoretical side of the controversy than has Sir Oliver Lodge. After referring to Volta's experiment of charging two insulated plates of different metals by contact, Lodge says:⁴¹

The mistake which has been, and still frequently is, made with regard to this simple and not very important experiment, has been to regard the charge as evidence of a peculiar E. M. F., at the point of contact, causing a difference of potential in the two metals. And this fictitious contact E. M. F. has then been appealed to to explain the voltaic battery.

The right way of regarding the matter is to consider the battery first, and explain its action chemically so far as it is possible to explain it at present; and then to point out that similar things will occur in air (an air battery, in fact), with the slight difference that since air is a dielectric instead of an electrolyte no continuous current is possible, but merely a slight electric displacement.

The effective cause of the whole phenomenon in either case is the greater affinity of oxygen for zinc rather than copper. This by itself would cause a greater strain of negative electricity towards zinc—a slackening of the negative cords in it, to speak in the language of the cord model—and a consequent rise of the negative potential. A piece of isolated zinc is therefore some 1.8 volts below the potential of the atmosphere. The same sort of thing is true for copper except that the intensity of the strain is less, as evidenced by the less heat of formation of CuO as compared with ZnO; and accordingly a piece of isolated copper is about 0.8 volt below the potential of the atmosphere.

Directly the two metals touch they necessarily become of the same potential—all parts of a conductor are at one potential unless there are disturbing internal forces—and the equalization of potential is effected by the rush of electricity across the junction, whereby the zinc receives a positive charge and the copper a negative charge until their potential is equalized. In air the equalization is effected in an instant. In water it is a matter of eternity. That is all the difference. The

⁴¹ "Modern Views of Electricity," p. 111.

thing observed in the Volta effect is not a difference of *potential* between zinc and copper, but a difference of *charge*; the two metals being charged so as to make their potential uniform.

It is, perhaps, better to leave the question of the differences between the phenomenon of the contact charging of metals and the charging of a metal in an electrolytic solution for a later discussion, but it seems important to call attention here to the fact that the metal which loses electrons and becomes positively charged by contact with another metal is the one which gives off positive ions and becomes negatively electrified in an electrolytic solution.

It seems necessary, also, to protest against the common use of a potential difference as an explanation of an electric transference. A potential difference is not a cause; it is only the expression for the magnitude of an effect, just as the weight of a body is an expression for the magnitude of the gravitation stress upon it, not an explanation of gravitation.

But, passing over this phase of the question, the one fact which the writer is able to make out from the above quotation is that Lodge regards as the fundamental cause of contact electrification "the greater affinity of oxygen for zinc than for copper," and that he regards this explanation as contradictory of Bennett's hypothesis that "Different bodies have different capacities for holding the electric fluid" rather than confirmatory of it. For if the oxygen ion which combines with metals is always negatively electrified, as is universally believed, a greater affinity for the electric fluid would imply a greater affinity for oxygen, and *vice versa*. Lodge apparently recognizes this fact, but he regards the affinity for oxygen as the primary phenomenon and the attraction for the negative charge of the oxygen as secondary. Thus he says, speaking of the greater affinity of oxygen for zinc, "This by itself would cause a greater strain of negative electricity towards zinc." It would thus seem that Lodge believes with Bennett that copper has a greater capacity for holding the electric fluid than has zinc, but that this is caused by the greater strain of negative electricity toward the zinc, and this, in turn, is caused by the greater affinity of oxygen for zinc. This explanation seems to the writer to have two important objections not found in Bennett's hypothesis, in that it involves two more guesses which may not be correct.

If affinity for oxygen is understood to mean an attraction for the negative charge of an oxygen ion, the fundamental distinction between the two points of view must largely disappear. If zinc combines more readily with oxygen than does copper it may be because the negative oxygen ion is more strongly attracted by positive zinc ions than by positive copper ions, or it may be, as Fabroni believed, because the zinc ions may

more readily escape from the metal surface to combine with oxygen ions than may the copper ions. That is, what seems to be the greater attraction between zinc and oxygen than between copper and oxygen may mean merely that the cohesion of copper for its positive ions is greater than the cohesion of zinc for its positive ions. In either case zinc would oxidize more readily than copper, and the heat of combination with oxygen, which is the difference between the work required to separate a gram of the metallic ions from the metal surface and the heat generated by the combination of these free ions with negative oxygen ions, would be greater for zinc than for copper.

Lodge does not attempt to describe the physical changes by which he assumes the zinc when insulated and in contact with an oxidizing medium to lose its power of retaining its electrons, but such an explanation has been attempted by various physical chemists. Thus Knoblauch⁴² has proposed an explanation as follows: The metals are covered by an adsorbed water film. This water film contains oxygen from the air, and consequently oxidizes the surface of the metal, forming a solution of the metallic oxide. This oxide dissociates in the water into positive (metallic) ions and negative hydroxid ions. The negative ions have the greater diffusion velocities in the solution, and hence move away from the plate faster than the positive ions. Hence, when two metals are placed in contact the more oxidizable metals lose their negative ions by way of the water film faster than do the nobler metals and consequently become more positively electrified.

This explanation is at least intelligible, but unfortunately it does not accord with the facts, since when zinc and copper are connected by a water film the negative ions in the water do not go to the copper, but to the zinc. It is only when there is a metallic contact and no water contact between the metals that they take the charges observed by Bennett and Volta.

It has been shown many times that when the metallic surfaces are varnished or coated with paraffin, or even when they are prepared by filing or melting under melted paraffin and are not allowed to come in contact with the oxygen of the air or water, there is still a contact E. M. F. at their surface. Also, when plates of iron and platinum have been heated red-hot several successive times in an atmosphere of pure hydrogen, the hydrogen being removed after each heating, there is still an electromotive force between them when they are brought into contact.

It has been found that the magnitude of the charges taken by the metals may be greatly influenced by their surface condition and by the occlusion of gases, but when every precaution has been taken to remove the occluded gases the metals still take charges from each other on contact.

⁴² *Zeitschrift für physikalische Chemie*, 39, 225.

The charges which we have been considering appear only after the two metals have been placed in metallic contact, but if metals have characteristic charges, as do their electrolytic and gaseous ions, it should be possible to detect these charges without bringing the metals into contact. Thus, when a charged body is brought near an insulated conductor it induces a bound charge of opposite sign to its own charge and a free charge of the same sign as its own charge upon the insulated conductor. If the conductor be not insulated, the free charge escapes to earth, but the bound charge remains, retained by the presence of the inducing charge.

Since nothing but an electrical charge of the opposite sign may induce a bound charge in an adjacent conductor, if different metals are electrically neutral before being brought into contact with each other they will not induce free and bound charges upon each other before being brought into contact, but if they are already differently charged before being brought into contact, then each should induce both free and bound charges upon the other when they are insulated and placed near together.

That different metals do actually induce such charges upon each other while still separated was shown by Exner in 1881.⁴³

In this experiment a zinc plate was placed in a horizontal position upon insulated supports and was discharged to earth and then left insulated. A similar copper plate was also discharged to earth and then insulated and placed parallel to the zinc plate and close to it. While in this position the copper plate was connected to an electrometer in which it produced a deflection of +9 scale divisions, due to the free charge induced by the zinc plate. While still connected to the electrometer this free charge was discharged to earth, and the electrometer reading returned to zero. Then the copper plate, while still connected to the electrometer, was raised from the zinc plate, thus releasing its bound charge, and the electrometer showed a deflection of -9 scale divisions, due to the charge which had been bound by the zinc plate. After the copper plate had been removed, the zinc plate was tested and showed no free charge, it having been insulated throughout the experiment.

This experiment, which may be repeated in any laboratory, shows conclusively that a zinc plate which has been discharged to earth and insulated is still capable of inducing a free positive charge and a bound negative charge on a copper plate which is placed near it.

Exner also showed that when a platinum plate and a zinc plate, after having been discharged to earth and then insulated, are placed parallel and very near together each induces a free charge upon the other which may be shared with an electrometer. If the electrometer be connected first with the platinum plate it will show a positive charge. If the elec-

⁴³ "Repertorium der Physik," 17, 444.

trometer and plate are discharged to earth and again insulated and the electrometer be connected with the zinc plate, it will show a negative charge. After this has been discharged to earth and the plate again insulated, the platinum will again show a free positive charge, and so following. In this manner, Exner was able to take twenty successive charges, alternately positive and negative, from his plates before their induced charges wholly disappeared. This corresponds exactly to discharging alternately the conductors of an insulated, charged Leyden jar.

The free charges induced by the approach of different metals to each other are discussed at length by Majorana in the *Philosophical Magazine*, 48, 241, and are called by him the "approach charges," while the bound charges which appear only after the metals have been discharged to earth and then separated he calls the "separation charges." There is, however, no distinction to be made between these charges and the ordinary bound and free charges induced in conductors by adjacent charged bodies. It is plain that if the two metals be connected while close together each will retain its bound charge, but the free charges from both will combine. That is, the free negative charge will pass to the metal which has the free positive charge and the bound negative charge. After separation this metal will be negatively charged and the metal from which the electrons escaped will be left with a positive charge. These are the "contact charges" observed by Bennett and Cavallo and later shown by Volta.

Majorana also succeeded in showing the attraction of one metal for another due to their bound charges.

It is plain that these free (approach) charges cannot be accounted for by Knoblauch's chemical explanation. Neither can they be accounted for on the assumption of an electric double layer of any kind on the surface of the metal, since the distance between the positive and negative surfaces in such a double layer would necessarily be so small that their differential effect would vanish at distances too small to be observed, while the approach charges may easily be observed when two plates of different metals are more than a centimeter apart.

They may even be shown at a much greater distance by using a hollow conductor of one metal and introducing the other metal into it, when an induced charge may be taken from the outer surface of the hollow conductor while the inner metal is nowhere close to its walls. In this case, all talk of the double electric layer is excluded, since the introduction of equal positive and negative charges into a hollow conductor can induce no charge upon its external surface. Neither can any chemical action between the two metals produce this external charge, since any chemical action, such as is suggested by Lodge, would produce equal charges of positive and negative electrification.

In the experiments of Exner and Majorana the two metals were insulated and their free charges observed by allowing them to be shared with an electrometer, but if the point of view here presented be correct, greater bound charges will be induced upon the metals if they are in contact with the earth, so that their free charges may escape, than if they are insulated. Accordingly, if one of the metals be earthed it will induce a greater electric separation in the other metal than it will while insulated.

The most favorable condition for the absolute electrical neutrality of a conductor is when it is within a closed, hollow metal conductor and in metallic contact with its walls; but if the metals have characteristic charges, as do their atoms, they should still be capable of inducing charges upon each other, even under these extreme conditions. On the other hand, if they have only zero charges under these conditions, it seems impossible that they should be able to induce free charges in each other when brought near together.

The fact that one metal while under the conditions specified may induce a free charge in another insulated metal which has been discharged to the inside of the hollow conductor which contains them both has been shown by the present writer in the following manner:

A Dolezalek quadrant electrometer, *E* in Figure 25, was enclosed in a cage of fine wire mesh which was earthed through a wire soldered to the water system of the laboratory. The outer case of the electrometer and one pair of quadrants were connected to this cage. The other pair of quadrants was connected to a hollow cylinder of copper 15 cms. long and about 2 cms. in internal diameter. This cylinder, *C* in the figure, was supported horizontally upon hard rubber blocks inside the cage and parallel to one of its sides. The needle of the electrometer was supported by a quartz fiber and was charged from two hundred dry cells and left completely insulated during the experiment.

A round metal rod, about 1 cm. in diameter, *R* in the figure, was mounted in a metal guide, i. e., a hollow cylinder of brass supported outside the cage but projecting through it into the inside and soldered to it. This brass cylinder, which was just large enough to carry the metal rod, was concentric with the axis of cylinder *C*, so that the rod when pushed through it would pass concentrically through cylinder *C* and through a round hole in the opposite side of the cage.

Before beginning an experiment the hollow cylinder, *C*, was put into contact with the outer cage, so that the charge induced upon it by the electrometer needle might be taken off. When, now, the earthed metal rod was pushed through *C* a charge was induced upon *C* which was shared with the electrometer, and which varied with the metal of the rod. A compound rod made of two rods of zinc and copper of the same size put

together end to end concentric with their mutual axis was pushed through the cylinder; the electrometer needle was differently deflected according as the zinc or copper part of the rod was inside the cylinder.

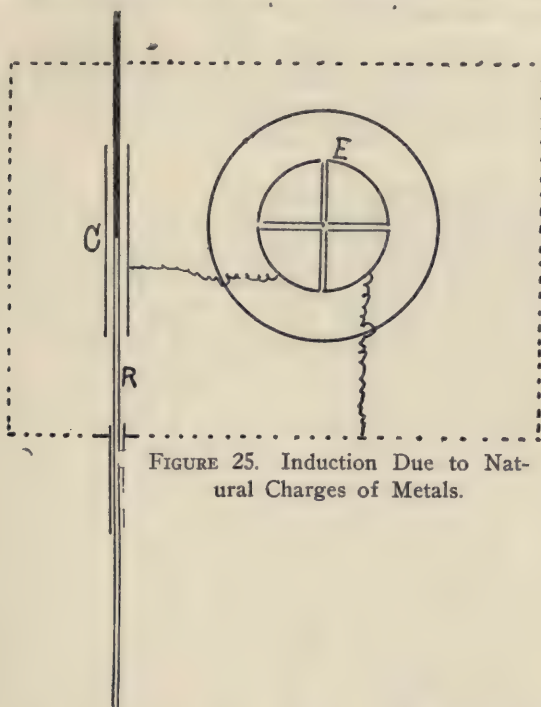


FIGURE 25. Induction Due to Natural Charges of Metals.

Thus in one experiment the copper part of the rod was pushed through cylinder *C*, *C* was then discharged to the cage, and the zinc part of the rod was pushed into it. As soon as the zinc had taken the place of the copper in the cylinder the electrometer showed a deflection of 12.5 scale divisions due to the free charge induced upon the cylinder, and this was repeated many times.

When the whole rod was withdrawn from *C* and an insulated copper rod of the same diameter substituted for it was connected alternately to the zinc and the carbon of a dry cell, the other pole being meanwhile connected to the cage, the electrometer gave a difference of scale reading of 35 scale divisions. Since the electromotive force of the dry cell used was about 1.25 volt, the difference of deflection for the zinc and copper was apparently due to a potential difference of about 0.4 volt between them, the zinc being electropositive to the copper by that amount. This difference remained unchanged when both the zinc and copper ends of the rod were connected with the outer cage.

By using an induction cylinder 2.5 cms. long instead of *C*, it was

found that the zinc was everywhere electropositive to the copper, but that on account of its bound charge it was most electropositive where it joined the copper, and that its electropositive charge decreased gradually with the distance from this junction.

Similar experiments were performed with compound rods of other metals, in some cases three different metals being used in one rod, but in every case each metal induced a different charge upon the surrounding hollow cylinder.

These experiments seem to show very definitely that a metal while in electrical contact with the earth or with the inside of a hollow conductor, although by definition at zero potential, still retains a certain characteristic charge which is capable of inducing an electric separation upon a different metal when brought near it. These characteristic charges I have ventured to call the Natural Charges of the metals.

When two metals are brought near together while in electrical contact with the earth their natural charges are increased or diminished by the bound charges due to their mutual induction. If insulated while near together and then separated, their bound charges become free charges. If then they are joined to earth such a transference of electricity will take place between each of them and the earth as will restore their original characteristic charges. Thus if plates of zinc and copper be connected to earth by wires while at a distance from each other and then be brought close together, while they are approaching electrons will flow from the earth to the copper plate, and from the zinc plate to the earth. If they be connected to each other, instead of to the earth, electrons will flow from zinc to copper as they approach each other, and from copper to zinc as they recede from each other.

If a metal be connected to the inside of a hollow conductor it will retain a bound charge due to the induction of the outer conductor, hence its charge will depend upon the nature of the outer conductor and will not be the same in hollow conductors of different metals, and in none of them will it be the same as when joined to earth at a distance from other conductors. It follows from this that when two metals inside a hollow metal conductor are brought into contact with each other and with the outer hollow conductor, the bound charges which they acquire are partly due to their mutual induction and partly to the induction of the outer hollow conductor. If they are flat plates and are placed parallel and very close together when they are touched to the outer conductor, their bound charges may be quite largely due to their mutual induction. If they are spheres with their surfaces touching while they are put into contact with the outer conductor, their bound charges will be determined principally by the induction of the outer conductor.

The effect of a hollow conductor upon the contact charges of two metals within it was shown by the present writer in an investigation published in 1912.⁴⁴ A polished zinc ball 5 centimeters in diameter was insulated by a short piece of silk thread and suspended by a cord which passed over a pulley so that the ball could be lowered into a hollow conductor and charged by contact with its bottom and then raised and discharged to a gold-leaf electroscope of the C. T. R. Wilson pattern. Copper and aluminium beakers of about 750 cc. capacity were used as the hollow conductors.

One of these beakers was placed below the zinc ball and earthed, and ten successive charges were taken from it by the zinc ball, which was raised and discharged into the gold leaf after each contact with the beaker. Then the other beaker was substituted, and a similar set of charges was taken from the inside of its bottom and shared with the gold leaf of the electrometer. The deflection of the gold leaf for each charge was read by a microscope and scale. As a mean of twenty sets of ten readings from each beaker, made in alternate sets of ten, the difference of the charges taken from the aluminium and copper beakers gave a difference of deflection in the gold leaf of 20.8 scale divisions, when the sensibility of the instrument was fourteen scale divisions for an ordinary dry cell.

A disc of tinfoil a little larger than the bottom of the beaker was then pressed down into each beaker until it rested upon the bottom and was turned up about one centimeter around the inside of the beaker. The zinc ball was then charged as before, but by contact with the tinfoil instead of the metal of the beaker. As a mean of twenty sets of readings for each beaker made exactly as before, the electrometer deflections amounted to twenty scale divisions for the difference of charge taken from the tinfoil inside the two beakers.

The beakers were then inverted and the tinfoil discs were placed upon the *outside* of their bottoms and the zinc ball charged by contact with these discs, as before. The mean of ten successive sets of readings taken in this way gave a difference of only 1.2 scale divisions as representing the difference in the charges taken from the tinfoil while resting upon the aluminium and copper beakers. This difference was not greater than the probable error of the experiment.

A third series of readings was then made with the beakers loosely wrapped over the outside with tinfoil, and the zinc ball was charged by contact with the inside of their bottoms as before in the first series. In this series the charges taken from the inside of the naked beakers gave a difference of deflection of 23.4 scale divisions per set, but only 7.5 scale divisions per set when they were wrapped in the tinfoil. In this case,

⁴⁴ *Physical Review*, 35, 484.

since the bound charges induced upon the two beakers by the tinfoil wrapping were different from their normal charges in the earth's field, the charges which they, in turn, induced upon the zinc ball were different from the charges which they induced with the tinfoil wrapping removed.

The above experiments seem to show conclusively that contact electrification is not due to chemical action between the opposed metals and the surrounding atmosphere, in which case the charges should be independent of the surrounding hollow conductor, but that different metals when in contact with the earth, and, by definition, at zero potential, still retain characteristic charges which are capable of inducing charges upon other conductors when brought near to them.

Since the most electropositive ions in electrolysis are from the metals which are most electropositive in the contact series, it would seem that the characteristic charges of the atoms determine the position of a metal in the contact electric series as they do in the cohesion series. Hence these two series must run parallel, as was shown in Table IV.

THE ELECTRICAL CHARGE OF THE EARTH

We have spoken of the charges which metals take when at a distance from other conductors and in good electrical contact with the earth as the "natural charges" of the metals, but it must seem extremely probable from what has preceded that these natural charges are modified by the bound charges which the metals take when in the general electric field of the earth.

We have taken the earth as our zero of potential, just as we have taken the sea level as our zero of altitude, but we have recognized both as arbitrary zeros. We have also taken the inside of a hollow conductor as a zero of charge, but we have shown that the bound charge upon a metal within a hollow conductor depends upon the material of the hollow conductor.

The fact that we may have a conductor in such an electrical condition that it will take electrons from the earth shows plainly that the earth has a supply of the electric fluid which may be drawn upon at will. This was a fundamental assumption in Franklin's theory and the later theories which were based upon it, as, for example, the Cavendish theory, which will be considered later in this paper.

When the two-fluid theory of electricity came to the front, the earth and unelectrified bodies in general were assumed to contain equal quantities of the two fluids, which were supposed to be combined or related in some way so as to neutralize each other's attractions and repulsions. It was also an essential part of this theory that equal quantities of the two fluids were transferred in every case of electric charging. In discussing this phase of the theory Maxwell says: ⁴⁵

⁴⁵ "Electricity and Magnetism," 3d ed., 1, 40.

The introduction of the two fluids permits us to consider the negative electrification of A and the positive electrification of B as the effect of *any one* of three different processes which would lead to the same result. We have already supposed it produced by the transfer of P units of positive electricity from A to B , together with the transfer of N units of negative electricity from B to A . But if $P + N$ units of positive electricity had been transferred from A to B , or if $P + N$ units of negative electricity had been transferred from B to A , the resulting "free electricity" on A and B would have been the same as before, but the quantity of "combined electricity" in A would have been less in the second case and greater in the third than it was in the first.

It would appear therefore, according to this theory, that it is possible to alter not only the amount of free electricity in a body, but the amount of combined electricity. But no phenomena have ever been observed in electrified bodies which can be traced to the varying amounts of their combined electricities. Hence either the combined electricities have no observable properties, or the amount of the combined electricities is incapable of variation. The first of these alternatives presents no difficulties to the mere mathematician, who attributes no properties to the fluids except those of attraction and repulsion, for he conceives the two fluids simply to annul one another, like $+e$ and $-e$, and their combination to be a true mathematical zero. But to those who cannot use the word fluid without thinking of a substance it is difficult to conceive how the combination of the two fluids can have no properties at all, so that the addition of more or less of the combination to a body shall not in any way affect it, either by increasing its mass or its weight, or altering some of its other properties. Hence it has been supposed by some that in every process of electrification exactly equal quantities of the two fluids are transferred in opposite directions, so that the total quantity of the two fluids in any body taken together remains always the same. By this new law they "contrive to save appearances," forgetting that there would have been no need of the law except to reconcile the "Two Fluids" theory with facts, and to prevent it from predicting nonexistent phenomena.

While we now know with certainty that no such double transference of electricity takes place in charging or discharging a body, the notion of electric neutrality which was based upon this conception of electric transference still plays a prominent part in the electrical theories of the day.

From the standpoint of the Faraday theory, no isolated body could have an electric charge, and accordingly the earth was of necessity electrically neutral.

If the assumption of the electric neutrality of the earth is essential to the explanation of electrical phenomena, then we are justified in making it; but it then becomes merely an hypothesis invented to aid in explaining phenomena which seem to us to be otherwise inexplicable. Even in that case, however, the hypothesis should be tested experimentally if possible, and if the experimental evidence is unfavorable to our hypothesis the adequacy of our theory is to that extent thrown into doubt.

From our present knowledge of electrical phenomena we are compelled to believe that material bodies contain both particles of matter (material sub-atoms) and particles of electricity (electrons). It seems

also to be definitely established that material atoms, as we know them, consist of both the positive (material) sub-atoms and electrons. It is also well known that certain material particles known as alpha-particles enter into the constitution of a considerable number of atoms, and the relations of the periodic law seem to indicate that the elementary atoms of which all known physical bodies are constructed are built on one general plan and presumably of the same materials. This assumption is greatly strengthened by the discovery of the X-ray spectra of all the elements and their definite arrangement in a linear series with the atomic numbers.

It is known that elementary alpha-particles and electrons may combine to form a gas molecule which has no appreciable electric field, so it seems possible that there may have been in the beginning just a sufficient number of alpha-particles and other positive sub-atoms in the earth to combine with the electrons and form electrically neutral atoms similar to the helium atom.

It is well known, however, that the earth is not built up of such electrically neutral atoms. No part of electrical theory has more evidence in its favor than the hypothesis that the forces known as affinity, cohesion and adhesion are electrical attractions between the positive sub-atoms and electrons of molecules, and no such forces could exist if the atoms were electrically neutral in the sense in which that term has been used in electrical theory. It is because the helium atom approximates such electric neutrality that it remains uncombined.

But even the neutrality of the helium atom is not necessarily the kind of neutrality which was postulated in the two-fluid theory. We call a body electrified when we can detect a difference in the electrical properties of the surrounding medium close to it and at a distance from it, that is, when it produces a field of strain in the elastic ether which is different from that around uninsulated conductors. If the elastic ether is already in a condition of strain about the earth, then an "electrically neutral" body is one around which the ether strain is the same as it is in the field of strain of the earth, and not one about which there is no ether strain at all.

When we consider the experimental evidence for and against the electric neutrality of the earth we are at once struck by the fact that the electrical condition of the earth is apparently not even stable. For example, radioactive changes are taking place in the earth, and apparently in the atmosphere. There are indications that these changes have been more important in the past than they are at the present time. In some of these changes the negative electrons are sent off at very high speeds, and it seems probable that some of them have escaped from the earth.

On the other hand, it is not improbable that the earth is receiving electrons from the sun. There are evidences of extensive radioactivity,

or at least of extensive dissociation of atoms, on the sun, and there are reasons for thinking that streams of electrons are being discharged from the sun to the earth. The aurora is generally attributed to a discharge of electrons taking place toward the earth through the very highly rarefied upper atmosphere. No equivalent discharge in the opposite direction is known.

In this connection Sir Oliver Lodge says: ⁴⁶

The Earth is in fact a target exposed to cathode rays, or rather to electrons emitted by a hot body, viz., the sun.

* * * * *

The gradual accumulation of negative electricity by the earth is a natural consequence of this electric bombardment extending to greater distances across space, where no residual matter exists; and the fact that the torrent of particles constitutes an electric current of fair strength, gives an easy explanation of one class of magnetic storms; these storms having long been known, by the method of concomitant variations, to be connected with sun spots and auroras.

The phenomenon of radioactivity, itself, seems to indicate that the electrical conditions on the earth have changed since the present unstable atoms were originally formed. If the atoms consist of electropositive parts combined with electrons, the characters of the groups which constitute the atoms were determined in the beginning by the relative numbers of electrons and positive sub-atoms. If this relation should change with time, certain of the original combinations would become unstable. Thus, if an additional supply of electrons should be received by the earth, these might combine with the most electropositive atoms, or these latter might set free some of their loosely held positive sub-atoms which would then combine with the excess electrons. In fact, the changes which are supposed to occur in the successive disintegration of radium indicate that there are more alpha-particles than electrons set free, although two electrons are required to neutralize the positive charge of one alpha-particle. Thus in the complete disintegration series of uranium as given by Soddy,⁴⁷ there are seven alpha-particles and four electrons set free. In several changes only alpha-particles are given off. If the atom was neutral before the alpha-particle was given off, it must have been negatively charged afterward, yet no less than four successive changes of this kind are shown, beginning with the parent of radium and ending with radium-A. A similar relation seems to hold between the numbers of alpha-particles and electrons set free in the thorium and actinium disintegrations.

Aside from the above argument, we have strong experimental proof that the earth is an electrically charged planet. It is well known that the

⁴⁶ "Electrons," p. 168.

⁴⁷ "The Interpretation of Radium," p. 205.

electric potential rises rapidly with distance above the earth. Within the range of most observations this change is very irregular, though usually in the same direction. This irregularity has been attributed to the irregular distribution of charges on clouds in the earth's atmosphere, which, in order to account for the observed rise of potential, must usually be positively electrified. Observations made in the highest balloon ascensions still show a rise of potential which seems to tend toward a constant value. From the sixteen recorded observations on the rise of potential at heights between two and three miles which the writer has been able to find, the average rise is 10.7 volts per meter. The nine recorded observations above three miles give an average of 7.1 volts per meter. Two of these were at heights of approximately four miles, and were respectively 8.4 and 7.9 volts per meter.

These numbers are undoubtedly too small, since in none of the recorded ascensions has there been suitable provision for discharging the balloon. In ascensions to the height of four miles the balloon, unless discharged, would be negatively charged to about 200,000 volts as compared with the air at the same elevation. Since the measurements have regularly been made at a distance of only a few meters below the balloon, the error due to the charge of the balloon has probably been considerable.

If it be assumed that the number of positive sub-atoms in the earth is just sufficient to "neutralize" the charge of the electrons, then there must be a great excess of positive sub-atoms in the upper layers of the atmosphere to account for the observed rise of potential. The observations which have been made on the auroral light seem to indicate that the reverse of this is the case. Hann⁴⁸ regards it as definitely established that auroras may be as high as 125 miles. Arrhenius⁴⁹ quotes as among the best measurements of the heights of auroras those made by Paulsen in Iceland, which were made by the use of two theodolites at distant stations which were connected by telephone, and which gave as the maximum height of the polar light about 250 miles. The only reasonable explanation yet proposed for the aurora is that it is due to the discharge of negative electrons toward the earth through the rarefied upper air. This would indicate that the upper limits of our atmosphere are still negatively electrified with reference to the earth.

The hypothesis of the negative electrification of the earth is not new. In 1879 Rowland⁵⁰ proposed practically the above theory of the aurora, based upon the assumption of the negative electrification of the earth's atmosphere. In 1881 he presented the same theory to the Congress of

⁴⁸ "Lehrbuch der Meteorologie," S. 4.

⁴⁹ "Lehrbuch der kosmischen Physik," S. 912.

⁵⁰ "Physical Papers," p. 179.

Electricians in Paris. In this report he said that Lord Kelvin believed the earth to be negatively electrified, and he proposed to the congress that this question be made a subject of international investigation.

In a paper on "Electricity in the Atmosphere,"⁵¹ Y. Homma discusses some of the attempts to explain atmospheric electricity by ionization of the air or by radioactive materials in the earth, and says:

After all it seems to me that the ion theory by itself is not quite competent to account for several phenomena in atmospheric electricity. The existence of the free ions in the atmosphere is beyond dispute. That they would exercise some influence on the phenomena of atmospheric electricity is also quite evident. But it is doubtful whether the part they play would be so essential or primary. Possibly they act rather as a disturbance factor in the field of atmospheric electricity, whose primary existence must be accounted for by some other theory.

Homma concludes that the absolute potential of the earth must be of the order of 10^6 volts to account for the phenomena of atmospheric electricity.

Another indication of the charge of the earth has been mentioned by Deslandres and Bosler, *Science Abstracts A*, 13, 413, in the observations on Comet Halley. The abstract says:

Examination of the observations of the position of the tail streamers made at the Johannesburg Observatory leads to the probability of the deflection of the tail being due to its having suffered electrical repulsion by the earth.

The above references have been given, not because of their authoritative character, for scientific facts are not established on the authority of great names, but to show that there is a widespread belief among intelligent physicists, based upon experimental evidence, that we are living on an electrified, and not an electrically neutral, planet.

Another argument for the electrical charge of the earth is the difficulty, if not impossibility, of accounting for its magnetic field on any other hypothesis. Since Rowland's experiments on electrical convection, in which he established experimentally that a rotating electrified body has a magnetic field, there have been numerous attempts to account for the earth's magnetic field on the assumption that the earth has a negative charge. Rowland was apparently the first to propose this hypothesis, but after calculating the magnitude of the charge required he abandoned the theory on the ground that the necessary charge must be unbelievably great. Since that time, other physicists have returned again and again to this hypothesis as offering the only conceivable explanation. Thus Sutherland says:⁵²

⁵¹ *Terrestrial Magnetism*, 12, 49.

⁵² *Terrestrial Magnetism*, 5, 73 (1900).

A possible cause of the earth's magnetism is the rotation of an electrostatic field within the earth, as Rowland's experiments have proved that a moving charge of electricity produces a magnetic field analogous to that of a current. If the earth carries round an electrostatic field in its rotation, then it will have the axis of its magnetic field identical with its axis of rotation, which is the chief approximate fact of the earth's magnetism. The actual obliquity of the magnetic to the rotational axis is traced to the unsymmetrical magnetic permeability of the earth, which also causes the induction of earth currents, the secular variation of whose tracks is the cause of the magnetic secular variation.

Sutherland computes the negative charge which the earth would have to carry on its surface in order to account for its magnetic field, and finds it to be 17.10^7 electromagnetic units or 51,000 electrostatic units.* He thinks it improbable that the earth has such a strong electrostatic field as this would produce, and hence concludes that there is a correspondingly great positive charge at the center of the earth which neutralizes its external electric field.

Realizing the improbability of an electric charge of this magnitude being retained at the center of the earth, and, perhaps, also the difficulty of keeping the two charges apart in a conducting sphere, he later modifies his theory by assuming that the positive and negative electricities of the earth are arranged in concentric layers with the positive electricity on the inside. He conceives that this condition may be brought about by all the molecules of the earth being so oriented that their positive charges are on the side toward the center of the earth and their negative charges on the side toward the surface. He says: ⁵³

Thus we have found that if the negative and the positive electricity in the earth are spread over concentric spheres whose radii differ by only the diameter of a single molecule, they can account for the earth's primary magnetic field. This separation of the two electricities would produce no external electric effect.

It is hard to say which of the two hypotheses proposed by Sutherland to account for the supposed electrically neutral condition of the earth is the more improbable. It goes without saying that if the earth is not electrically neutral neither of them is needed.

Since the publication of Sutherland's papers there have been numerous discussions of the probability of the earth's magnetic field being due to the rotation of a negative charge. The view that it is so caused has been strengthened by Hale's discovery of the similar magnetic field of the sun.

The most extensive recent discussion of the earth's magnetism is found in a series of papers published by Bauer in *Terrestrial Magnetism* during the year 1912. After discussing all the proposed causes, Bauer rather reluctantly, as it seems, comes to the conclusion that the earth must be actually electrified. Thus he says: ⁵⁴

* This seems to involve an arithmetical error.

⁵³ *Terrestrial Magnetism*, 8, 51.

⁵⁴ *Terrestrial Magnetism*, 17, 136.

It is of added interest that not only do the general facts of the earth's magnetism require that the outer rotating charge be negative, but that the facts disclosed by atmospheric electric instruments likewise require a surface negative electric charge, the source of which has not yet been satisfactorily explained. It is possible that the latter may represent a residual quantity, *viz.*, instead of an exact balance of the two opposite charges as assumed in deriving our magnetic potential expression, may there not be a preponderance of one charge, *e. g.*, the negative one, over the other?

Aside from the explanation of the earth's primary magnetic field, there are numerous magnetic variations or perturbations upon the earth which are quite universally attributed to electric currents in the earth's crust or in the atmosphere. Some of these are of a secular character and of entirely unknown origin; others are of a seasonal nature and indicate a shifting of the earth's charge or currents with the change in the inclination of its axis to the sun; still others are oscillatory in their character and of such short period that they have been named magnetic pulsations.

In these magnetic pulsations certain periods seem to occur more frequently than others. Several different observers have at various times noted pulsations of periods of about 12 seconds or about 30 seconds. Eschenhagen believes he has recorded beats between trains of oscillations of a period of 34 and 43 seconds. Birkeland has collected material to show that similar pulsations may occur at the same time over a region of 1200 miles across. H. Ebert, who has probably done the most accurate work in the measurement of these pulsations, has recorded series of them with as short a period as 0.025 second, and has shown that they were markedly independent of local weather conditions.

Oscillations of such short period occurring simultaneously over large regions cannot well be accounted for on the assumption of electric currents. They are much more of the character of the oscillations of an electric charge upon a conductor. Ebert discusses the probability of their being due to the oscillations of the earth's electric charge. After giving Thomson's and Lampa's calculations of the period of oscillation of a charge upon a conducting sphere, Ebert says: ⁶⁵

The earth presents a sphere freely floating in space, surrounded by air on all sides, with a surface of good conducting material. If one supposes its electrical equilibrium to be disturbed by any process within or without the earth, it can return to equilibrium only through a series of oscillations. The period of these oscillations computed according to the above formula is 0.15, or 1/6 to 1/7 sec.

The wave-length of this oscillation in air is equal to 46,130 km., *i. e.*, equal to 1.155 times the circumference of the earth, and hence not to be confused with the wave-lengths used in wireless telegraphy. It would be premature to state that a short oscillation of just this period appears especially often in the observations;

⁶⁵ *Terrestrial Magnetism*, 12, 13.

in order to make this certain the observations must be extended over a much greater interval of time, and verified in other places, under other conditions and with different apparatus. Should by such means this supposition be verified, another way would at once be pointed out, by which presumably a substantial new glimpse into the character of terrestrial magnetic disturbances would be afforded.

It seems then that the experimental evidence is in favor of the earth's being a negatively electrified planet, and that the hypothesis of its electric neutrality was based upon a theory of electrification which is no longer tenable. Such being the case, it must induce bound charges upon uninsulated conductors in its field, but the characteristic or natural charges of the elements must still be dependent upon their own structure, while all are modified alike by the earth's induction.

CHARACTERISTIC CHARGES AND SPECIFIC INDUCTIVE CAPACITY OF METALS

It has come to be the universal opinion of physicists that electrical attractions and repulsions are brought about by some condition in the luminiferous ether which is analogous to an elastic stress in material bodies. Faraday's classical experiment on specific inductive capacity showed definitely that electric attractions and repulsions are not of the nature of forces acting at a distance, but that they must be explained, if at all, by the properties of an all-pervading elastic medium. Thus Larmor says: ⁵⁶

According to any aether theory static electric attraction must be conveyed by elastic action across the aether, and an electric field must be a field of strain: hence each sub-atom with its permanent electric charge must be surrounded by a field of permanent or intrinsic aetherial strain, which implies elastic quality in the aether instead of complete fluidity: the proton must therefore be in whole or in part a nucleus of intrinsic strain in the aether, a place at which the continuity of the aether has been broken and cemented together again (to use a crude but effective image) without accurately fitting the parts, so that there is a residual strain all round the place.

Now it is well known that this "elastic" force of attraction or repulsion between electric charges is less in all material bodies than in the free ether, and that it is less in some bodies than in others. This seems to lead inevitably to the conclusion that the elasticity of the ether is weakened in the presence of material particles or atoms. Thus Larmor says: ⁵⁷

Each molecule individually, through the agency of its plastic field of force or aether strain, provides a yielding region in the aether in which the effective stiffness is diminished.

In a paper published by the present writer in 1911 ⁵⁸ the difference in

⁵⁶ "Aether and Matter," p. 26.

⁵⁷ *Astrophysical Journal*, 26, 120.

⁵⁸ "A Physical Theory of Electrification," Leland Stanford Junior University Publications, University Series, p. 42.

the contact electromotive force of metals was sought in the difference in their specific inductive capacities, it being maintained that the metals which are most electropositive in the contact series are those having the higher specific inductive capacities.

From this point of view, cohesion is weaker in the more electropositive members of a chemical series because their internal ether elasticity is less than in the more electronegative members of the group. Since the attraction between an electropositive sub-atom and an electron is proportional to the specific charge on the sub-atom and inversely proportional to the specific inductive capacity of the intervening ether, if the ether elasticity should decrease faster than the positive charge of the sub-atom increases, the attraction would be less the higher the charge of the positive sub-atom.

The principal objection to this hypothesis lay in the almost universal opinion of physicists that the specific inductive capacity of metals, if they can be said to have a specific inductive capacity, must be immeasurably great. In fact, in all our current electrical theory the specific inductive capacity of metals is taken as infinitely great; or, as it is frequently stated, metallic conductivity and specific inductive capacity cannot co-exist in the same substance.

This opinion is not based upon any experimental data, but upon the qualitative definition of specific inductive capacity proposed by Maxwell. Maxwell believed that electric induction consists of an actual displacement of the positive electrical condition (in the Faraday-Maxwell theory there was not necessarily any electric fluid whatever) in one direction and the negative electrical condition in the opposite direction in the ether. The greater the displacement for a given electromotive force and the greater the consequent separation of the two kinds of electrification, the greater the specific inductive capacity.

The elastic resistance which the ether offers to this electric separation was called by Maxwell the electric elasticity of the ether. The electric separation for a given inducing charge would then be inversely proportional to the electric elasticity of the medium in which the induction took place. Faraday had defined specific inductive capacity as directly proportional to the induction produced by a given charge, hence Maxwell's electric elasticity is necessarily the reciprocal of the specific inductive capacity.

Thus Maxwell says:⁵⁹

The analogy between the action of electromotive intensity in producing electric displacement and of ordinary mechanical force in producing the displacement of an elastic body is so obvious that I have ventured to call the ratio of the

⁵⁹ "Electricity and Magnetism," 3d ed., 1, 65.

electromotive intensity to the corresponding electric displacement the *coefficient of electric elasticity* of the medium. The coefficient is different in different media, and varies inversely as the specific inductive capacity of each medium.

Since from this definition the specific inductive capacity of a substance is the ratio of the displacement of an electric charge to the electromotive force which produces the displacement, and since the smallest possible electromotive force may produce a continuous electric displacement in a conductor, it follows from the definition that the specific inductive capacity of a conductor is infinite.

But we have learned since Maxwell's day that the smallest electromotive force may likewise produce a continuous electric displacement in the free ether; that is, that electrons in the ether outside of material bodies move with even greater freedom than in a metal, and that electric induction in a vacuum cannot consist in the displacement of the bound electricity in the ether, because there is no bound electricity in the ether. Accordingly since we are compelled to abandon Maxwell's explanation of induction and to look upon induction as something different from a displacement of bound electrical charges, there is no longer any ground for the assumption that the ether in a metallic conductor may not possess the property of specific inductive capacity. Whether it does possess this property, or not, is accordingly a matter for experimental determination.

The direct experimental determination of the specific inductive capacity of a metal is impossible by the ordinary methods, since the induced charges upon the metal itself mask the effect of the inducing charge upon other near conductors. The screening effect of an earthed metal conductor between a charged and an uncharged body is well known, but it is not necessarily a proof that electrical induction may not take place through the metal. It may equally well be explained by the hypothesis that the bound charge upon the earthed conductor has an equal and opposite inductive effect upon the uncharged body to that of the original inducing charge. This hypothesis is confirmed by the fact that the induction of a charged conductor upon an insulated conductor brought near it may be greatly weakened by placing an earthed conductor near the charged body on the side *opposite* to the insulated body. In this case we do not speak of electrical screening, but the effect is qualitatively the same as if the earthed body had been placed between the charged and the insulated bodies.

When a charged body is placed within an insulated hollow conductor its inductive effect upon bodies outside appears as great as when the hollow conductor is removed, but if the hollow conductor be earthed the bound charge upon it will wholly neutralize the inductive effect of the inner charge upon outside bodies.

If the hollow conductor be of very low conductivity, so that its bound charge requires an appreciable time to gather upon it, induction may take place through it while this charge is gathering, but will cease when the external conductor is fully charged. This phenomenon was shown in various ways in an investigation carried on in the Stanford laboratory by Miss Shirley Hyatt.⁶⁰ By making the whole or a part of the hollow conductor of a poorly conducting substance, as a thin silver film on glass or a tinfoil sheet cut into small squares with a razor, or by earthing it through a very poor conductor, an electroscope within the hollow conductor was made to show a deflection due to an external charge for a period of several seconds, or even for more than a minute, but in every case the hollow conductor became a perfect screen as soon as its bound charge had fully gathered.

These experiments seem to show that the ether within a metallic conductor may still possess the property which Maxwell regards as electric elasticity. The fact that cohesion may be very great in metals, whereas from our concept of the nature of cohesion it should be zero if the specific inductive capacity of the ether within the metal were infinite, is another argument in favor of a finite and not extremely high specific inductive capacity in metals.

While it is impossible to measure the specific inductive capacity of metals by determining the magnitude of the induction which may take place through them, it is possible to estimate its magnitude with a fair degree of approximation by means of other properties which vary with it. One of these properties seems to be cohesion, and since we have seen that the contact electromotive series varies as the cohesion series, we may expect the contact electromotive force of metals to vary with their specific inductive capacities.

Since this relation has not heretofore been stated for metals except by the present writer, it may be well to give a brief statement of the known facts upon which it is based.

In 1808, Reuss,⁶¹ of St. Petersburg, found that water in porous cells could be driven through the cell walls by an electric current, and that small particles suspended in water could be driven toward the positive pole by the current. The name Electric Endosmose was given to the phenomenon, and it was later very extensively investigated by Porrot, De la Rive, Becquerel and others, especially by Wiedemann.

In 1843, Faraday published the eighteenth series of his "Experimental Researches" under the title, "On the Electricity Evolved by the Friction of Water and Steam against other Bodies," in which he showed

⁶⁰ *Physical Review*, 35, 337 (1912).

⁶¹ "Wiedemann's Elektricität," 2, 181.

that pure water took a positive charge when in contact with nearly all solid substances with which it was tried, quill and ivory being the only exceptions observed. In paragraph 2099 he gives a list of thirty solids which were negatively charged by being placed in a steam-driven water spray. He found that turpentine oil when used as a spray usually gave positive charges to the bodies with which it came in contact.

In the same year Armstrong⁶² developed his hydroelectric machine, with which, by driving a spray of water by steam through a hole in a wooden plug, he was able to generate electric sparks 22 inches long.

Later, Quincke⁶³ undertook a very extensive series of investigations on electric endosmose, in which he found that by means of the high voltage given by an electric machine a column of water could be made to flow through a glass capillary tube in one direction over the surface of the column next to the glass and back in the opposite direction through the axis of the column. He found that water could be driven higher by a given electromotive force in a tube lined with shellac than in a glass tube, and that while water and alcohol in glass tubes flowed in the direction of the positive current, turpentine flowed in the opposite direction.

Quincke also found that particles of some twenty different substances all became negatively electrified when suspended in water, while most of them became positively electrified when suspended in turpentine.

Alfred Coehn⁶⁴ was apparently the first to relate these phenomena to the difference in specific inductive capacity of the liquids and solids with which they were in contact. He refers to the experiments of Tereschin,⁶⁵ who determined the heights to which water, methyl alcohol and ethyl alcohol could be driven in the same tube by a given electromotive force, and shows that these heights are very closely proportional to the specific inductive capacities of the respective liquids.

Coehn undertook the determination of the character of the charges produced on a large number of liquids of known specific inductive capacities when in glass tubes. He used a very high potential difference on his electrodes, and tested twenty-nine liquids. He found that twenty of these with specific inductive capacities greater than 5.1 took positive charges from glass with the single exception of propionic acid ($k = 5.5$), while nine liquids with specific inductive capacities less than 5.1 all took negative charges.

He then lined his capillary with sulphur and repeated his experiments and found all of the liquids except turpentine ($k = 2.2$) to take positive charges from sulphur.

⁶² *Philosophical Magazine*, 23, 194.

⁶³ *Poggendorff's Annalen*, 113, 513 (1861).

⁶⁴ *Wiedemann's Annalen*, 64, 217 (1898).

⁶⁵ *Poggendorff's Annalen*, 32, 333 (1887).

Coehn then stated the law: *Substances of higher dielectric constant take positive charges when in contact with substances of lower dielectric constant.*

In 1909 Coehn and Raydt⁶⁶ undertook the determination of the charges produced on various liquids by the measurement of the hydrostatic pressures against which they could be driven through capillaries of glass, quartz and diamond by a given electromotive force. They announced the following laws, which seem to be fully justified by the results of their investigation:

1. The electric charges on the liquid and capillary are proportional to their difference in specific inductive capacity.
2. Comparison of the dependence of change of level on conductivity showed that the results were not vitiated by this relation.
3. The change of level of mixtures of the liquids showed a regular variation from the one component to the other. The property is additive.
4. Determinations of change of specific inductive capacity with change of temperature agreed with the results of other observers by other methods.

It has been known for a long time that water spray in air takes a positive charge and that air bubbled through water leaves the water positively charged. In 1914 Coehn and Mozer⁶⁷ undertook an investigation on the contact electrification of gases by non-conducting and conducting substances. The gases were bubbled at a constant rate through the liquids and emerged against a net of platinum wire which was connected to a quadrant electrometer, the other quadrants of which were earthed through a condenser. They found that against the purest water that could be obtained the indifferent gases, oxygen, nitrogen and hydrogen, took negative charges in agreement with Coehn's former laws. Small traces of electrolytes led to smaller charges, and a sufficient concentration often led to a reversal of the sign of the charge. They found that when gases were bubbled through different liquids of known specific inductive capacity the positive charges left on the liquids were, in general, roughly proportional to their specific inductive capacities.

Finally, in 1915, Coehn and Franken⁶⁸ undertook to determine the charge given to a paraffin ball by various liquids in which the ball was immersed, then withdrawn and the liquid allowed to drain off. Their quantitative results were not very consistent, but they found that the paraffin ball always took a high negative charge from water, in some cases up to 135 volts, and that the addition of electrolytes to the water diminished the charge, as in the case of gases.

None of the methods used by Coehn and his students are applicable

⁶⁶ *Annalen der Physik*, **33**, 777 (1909).

⁶⁷ *Annalen der Physik*, **43**, 1048 (1914).

⁶⁸ *Annalen der Physik*, **48**, 1005 (1915).

to metals, but the results of their experiments seem to make it extremely probable that the contact charges of metals with non-metallic bodies and with each other are determined by their specific inductive capacities, and that if metals have the high specific inductive capacities which are usually attributed to them they should take positive charges from all other known substances.

It is possible to find many lists of substances arranged in the order of their electrification by friction or contact, but in all of these lists, except one⁶⁹ which has appeared since the experiments about to be described were performed, the metals are usually classed together about midway of the series given, usually between silk and india rubber. This location would seem to suggest that the specific inductive capacities of the metals lie near four.

However, since the metals may show considerable contact charges among themselves, it would seem that if Coehn's law may be applied to them they should be distributed throughout the contact series with non-metallic substances. Conversely, it would seem that if metals take their places distributed throughout the contact series with non-metallic substances we are justified in applying Coehn's law to them and in concluding that their specific inductive capacities are likewise distributed.

For the purpose of finding if this is the case, the experiments described below were undertaken by the writer in the summer of 1917 and a short paper on specific inductive capacity of metals was published in the *Physical Review* of August, 1918. The experiments and results which are given below are those which were described in the above mentioned paper.

Two methods were employed for testing the charges which were produced upon the metals by friction or contact. In one of these methods the conducting substances were mounted upon insulating handles, usually of ebonite, and the non-conducting substances were usually held in metallic forceps or tongs to avoid giving them charges by contact with the hand. The two were rubbed together, or merely placed in contact, and separated, and their charges were tested by a Wilson tilted electroscope, the plate of which was connected to one hundred dry cells. This gave the character of the charges and enabled one to tell whether the substances tested were close together or far apart in the contact series.

In the other method the metals to be tested were used in the form of rods. They were suspended from an insulating support and connected to one side of a four-microfarad paper condenser, the other side of which was joined to earth. After the rod had been rubbed or brushed with the

⁶⁹ P. E. Shaw, "Experiments on Tribo-Electricity," *Royal Society Proceedings*, Nov. 5, 1917.

substance with which the metal was being compared, the condenser was disconnected from the metal and discharged to earth through a ballistic galvanometer. It was hoped that this method might give comparable quantitative values, but such was not the case except in a very rough manner. It generally made it possible to determine the order of two metals fairly close together in the series, but even this was not always the case. Since surface conditions, temperature conditions, the method of rubbing or brushing the surfaces together, and perhaps other variations, may influence the magnitude of the frictional charges produced, it is very difficult to know that a set of non-metallic substances, as well as metals, are arranged in the proper order of their frictional electrification. Thus a polished surface is regularly electropositive to a matt surface of the same substance, a quartz surface parallel to the optic axis is electropositive to a surface perpendicular to the axis, and the like. Mercury may be made to take its place among the electropositive or the electronegative metals in the contact series. If a solid be immersed in mercury and withdrawn, the charge taken by the solid and by the mercury indicate that mercury comes between copper and tin in the contact series; but if any of the solids used in this investigation except the heavy flint glass rod at the positive end of the series be struck sharply upon a mercury surface it will take a negative charge from the mercury.

In testing a substance for its place in the series it was always tried with a considerable number of other substances, usually ten, or more, and some substances were tried with practically all the others. If the substances used were carefully discharged before trying them in contact with others, there was usually no conflict in the results obtained with different substances.

In order to make it possible to determine more closely a number of positions in the dielectric series, Professor Rogers, who was at that time engaged in measuring specific inductive capacities, kindly determined for me the specific inductive capacity of a number of the dielectrics used in the investigation. Where his values are used in the table they are followed by the letter R. The other values of specific inductive capacity used were taken from Landolt and Boernstein's tables. The results of the comparison of a number of substances for their place in the frictional or contact series are given in Table XXXVII, in which each substance took a positive charge from all those which precede it and a negative charge from all which follow it in the series.

TABLE XXXVII.

| Substance | k | Substance | k |
|------------------|---------|----------------------------|--------|
| Xylenite | — | Beeswax | — |
| Collodion film | — | Norway iron | — |
| Gun cotton | — | Nickel | — |
| Platinum | — | Khotinsky cement | — |
| Sheet rubber A | 2.1 R. | Quartz, matt face | — |
| Brass | — | Aluminium, oxidized | — |
| Iron pyrites | — | Silk | — |
| Celluloid sheet | — | Lead | — |
| Gold | — | Bismuth | — |
| Silver | — | Cadmium | — |
| Copper | — | Steel rod | — |
| Mercury (?) | — | Gelatine film | — |
| Tin | — | Cobalt glass | 4.32 R |
| Antimony | — | Quartz, + to axis | 4.5 |
| Sheet rubber B | 2.34 R. | Quartz, = to axis | 4.8 |
| Amber | — | Linen | — |
| Sheet rubber C | 2.59 R. | Aluminium, scratched | — |
| Sulphur disc | 3. R. | Flannel | — |
| Soft rubber tube | — | Zinc | — |
| Sheet rubber D | 3.14 R. | Boro-silicate crown glass | 6.2 |
| Copper oxide | — | Plate glass A | 7.6 R. |
| Ebonite plate | 3.02 R. | Calcite | 8.27 |
| Paper towel | — | Heavy silicate flint glass | 8.3 |
| Shellac | 3—3.4 | Chamois leather | — |
| Sheet rubber E | 4.2 R. | Heavy flint glass rod | — |
| Yellow oil cloth | — | | |

It will be seen from the above table that the metals take their places in the contact or frictional series with dielectric substances just as the latter do with each other. The natural inference to be drawn from this fact is that the position of a metal in the contact series is determined by its specific inductive capacity, just as is that of a non-metallic substance. This being true, we may state the following laws:

1. The specific inductive capacities of metals are of the same order of magnitude as are those of non-metallic bodies.

2. The more electropositive a metal is in the contact series, the higher is its specific inductive capacity.

INFLUENCE OF TEMPERATURE UPON SPECIFIC INDUCTIVE CAPACITY OF METALS

It has been known since the experiments of Cavallo that the contact charges of metals depend upon their temperature. It should follow that the charges which metals take from the earth, or what have been called in this paper the characteristic charges of the metals, should also vary

with the temperature. This hypothesis was verified by the method shown in Figure 25. In that experiment the metal rod, *R*, was turned down to a narrow neck about eight inches from one end, so that the two sections of the rod could be kept at different temperatures. Then when the two sections at different temperatures were alternately pushed into the induction cylinder, *C*, the electrometer deflections showed that they were differently charged relative to each other, though both were in metallic contact with the earth.

In the case of iron, steel, copper, brass and tin the warmer part of the rod was electronegative to the colder part; in aluminium the warmer part became markedly electropositive, while in zinc the difference was very slight.

Since the Thomson effect in iron indicates a change in the direction of the electromotive force at the junction of a cold and a hot part at about 150 degrees, an attempt was made to heat one end of a steel tube and keep the other end cold and measure the change of induced charge with a change of temperature. It was found that the tube used became more electronegative as its temperature increased up to 150 degrees, or more. From 150 to 200 degrees the electric charge of the metal changed very little, but beyond 200 degrees the tube became more electropositive with an increase of temperature. It was impossible to measure the induction of the tube much beyond 200 degrees, since at higher temperatures the hot tube ionized the air and allowed the induced charge of the cylinder to discharge to the tube.

It would seem to follow from this experiment that the internal cohesion of the steel tube should increase with an increase of temperature up to about 150 degrees and should then decrease with a further increase of temperature. When this deduction from the theory here given was first made by the writer it seemed an argument against the theory and was so presented to his classes, as it seemed improbable that iron, which softens at temperatures of only a few hundred degrees, should have its cohesion increased by heating up to 150 degrees; but a careful search through the literature of the subject showed that this phenomenon had already been observed.

In a series of experiments made by C. Bach and described in *Zeitschrift des Vereins deutschen Ingenieure*, 1904, p. 1300, the tensile strength of iron was found to be much greater at 200 degrees than at 20 degrees. From 200 to 300 degrees it decreases, but it is still greater at 300 degrees than at 20 degrees. At 400 degrees it is only a little less than at 20 degrees.

In the *Valve World* of January, 1913, is an article by I. M. Bregowski and L. W. Spring on "The Effect of High Temperatures on the

Physical Properties of Some Metals and Alloys". In this article it is shown that samples of cast iron, both soft and hard, have a greater tensile strength at 300 F. than at 70 F., and that at 750 F. the tensile strength is still within one per cent of as great as it is at 70 F. In the case of a sample of Crane Ferrosteel the tensile strength is greater at 750 F. than at 70 F.

In a dissertation by A. Lantz, entitled "Einwirkung der Temperatur auf die Biegefähigkeit von Flusseisen und Kupferdrahten," Berlin, 1914, the author finds that what he calls the *Biegefähigkeit* of iron, *i. e.*, its malleability or toughness as measured by the number of times it can be bent short forward and backward at a given point before breaking, increases with the temperature to about 220 degrees and then decreases. In some cases the wire would stand twice as many short bendings at 220 degrees as at room temperature, while at 350 degrees it would stand only one-fifth as many as at room temperature. The toughness of copper measured in this way continued to increase to 320 degrees, which was the highest temperature of the experiment.

In *Science Abstracts*, A, 20, 1190, is reference to an article by F. A. Epps and E. O. Jones (*Metallurgical and Chemical Engineering*, 17, 65-71, July, 1917) on the "Influence of High Temperature Upon the Elastic and Tensile Properties of Wrought Iron," in which the writers found that the ultimate strength appears to increase as the temperature increases from 70° F. to between 350° and 550° F. From the temperature of maximum strength the tenacity diminishes rapidly to 1000° F. The greatest gain over the strength of the metal at 70° was at 430°, where the gain in strength was 37.6%.

The above-mentioned experiments all seem to indicate that the cohesion of iron increases with its increase of temperature so long as the iron continues to become more electronegative, and that the cohesion begins to decrease at about the temperature at which the iron begins to lose its negative charge.

Specific Inductive Capacity and the Voltaic Cell

The hypothesis has already been advanced in the present paper that the electromotive force of a voltaic cell is due to the difference in cohesion of the two electrodes, the metal which has the weaker cohesion, and which accordingly dissolves more readily in water, becoming the electronegative pole of the cell. Since we have now shown that the cohesion series is the reciprocal of the contact electromotive series and that the latter series is determined by the dielectric series, we can understand the reason for the high dissolving and dissociating power of water. When a metal is placed in water, its surface atoms are partly

surrounded by water of specific inductive capacity 80, while the specific inductive capacity of the metal is not more than five or six. This must correspondingly weaken the cohesion of the metal for its surface ions, and some of these break away and escape into the water. Thus the specific inductive capacity of the solvent, as well as that of the metal, helps to determine the rate of escape of the positive metallic ions.

If this be true, it should be possible to construct a cell having both electrodes of the same metal placed in liquids of different specific inductive capacities. Such a cell has been known since the time of Davy, but no satisfactory explanation of its electromotive force has been given until the one here proposed. If the explanation here given is correct, the electrode in the liquid of higher specific inductive capacity will lose positive ions more rapidly than the other and will accordingly become electronegative with respect to the other.

This hypothesis has been fully substantiated by Mr. Dayton L. Ulrey in an investigation which furnished the material for his doctor's dissertation at Stanford, and which was published in the *Physical Review*, 12, 47-58 (1918). Mr. Ulrey says in concluding his paper:

1. The potential difference between electrodes of the same kind in a two-solution cell has been measured for a number of different percentage mixtures of two liquids for four different cases, and in each, after disturbing influences were removed, is shown to be strictly proportional to the difference in the specific inductive capacities of the two solutions.

2. In the two cases investigated with copper electrodes, one with platinum and six with calomel electrodes, the direction of the electromotive force of the cell is in accordance with the theory that the loss of ions from an electrode is dependent upon the specific inductive capacity of the electrolyte rather than upon the concentration of those ions in the electrolyte and a solution tension of the electrode.

The measurement of the specific inductive capacity of electrolytic solutions is beset with great difficulties and but few successful direct measurements of this kind have been made. The belief in the high specific inductive capacity of metals which has hitherto been held has given the basis for the assumption that the specific inductive capacity of an electrolytic solution must be greater than that of the solvent. However, if the metals have specific inductive capacities much lower than that of water, as our experiments seem to show, the presence of metallic ions in water should lower its specific inductive capacity, and a metal should go into solution more rapidly in pure water than in water containing metallic ions in solution. That such is the case is shown in the well-known phenomenon of the concentration cell.

It has also been shown that the electropositive metals have higher specific inductive capacities than the electronegative metals, hence the

presence of electropositive metallic ions in a solution should lower the specific inductive capacity of the solution less than the presence of the same number of electronegative metallic ions: Hence if equimolecular solutions of two metallic salts having the same acid ion but different metallic ions be used in a two-fluid cell having electrodes of the same metal, the electrode in the solution containing the more electropositive metallic ion should become the electronegative pole of the cell.

This hypothesis was verified by the writer for electrodes of four different metals in equimolecular solutions of zinc and copper sulphate, and was verified for a large number of different equimolecular solutions in an investigation carried on in the Stanford laboratory in 1915 by Miss Florella K. Finney.⁷⁰ Miss Finney says:

The results of the investigation show that the metals can be arranged in a series in the order in which the presence of their ions in a water solution affects the solution tension of a metal when placed in the solution. Furthermore, this series is the same as the contact electromotive series. That is, if both electrodes be of the same metal, the electrode in the solution which contains the more electropositive ion has the higher solution tension and accordingly corresponds to the zinc electrode, while the electrode in the solution which contains the less electropositive ion corresponds to the copper of the ordinary Daniell cell. The order of this arrangement of the metals was determined to the satisfaction of the writer as follows: Potassium, sodium, ammonium, barium, calcium, zinc, nickel, hydrogen, copper and ferric iron.

Miss Finney also found the same relation to hold when the same metallic ion was combined with different acid ions in the two solutions. She says:

Solutions of the chlorides and bromides of potassium and sodium and the iodide of potassium all agreed in showing that the solution tension of a metal is greater in the presence of iodine ions than in the presence of bromine ions, and is greater in the presence of bromine than of chlorine ions.

The significance of the above statement may be seen from the fact that the tables give the specific inductive capacity of chlorine as 2, bromine as 3.1 and iodine as 4.

The conclusions of Miss Finney were confirmed by the later work of Mr. Philo F. Hammond,⁷¹ who measured by another method the potential difference between electrodes of the same metal in equimolecular solutions containing different metallic ions with the same acid ion.

At the time of this writing an investigation is being carried on in the Stanford laboratory by Mr. George R. Harrison upon the magnitude

⁷⁰ *Physical Review*, 6, 400 (1915).

⁷¹ "The Influence of the Metallic Ions in an Electrolytic Solution Upon the Electrical Potential of a Metal Placed in the Solution." A thesis presented to the Department of Physics, etc. The New Era Printing Company, May, 1916.

of the static charge produced upon various metals by contact with dielectric liquids of known specific inductive capacities. Mr. Harrison's work has already been carried far enough to show that Mr. Ulrey's conclusions are verified for the static charges left upon metals by the liquids, and that the magnitudes given for the specific inductive capacities of metals by Table XXXVII, are apparently in close agreement with facts.

THEORETICAL CONSIDERATIONS

In order to assist in the presentation of the point of view toward which the phenomena described in this paper seem to lead, as well as to gain a clearer comprehension of our present electrostatic theory, if we may be said to have one, it seems important to consider very briefly the theories of the past and the causes which led to their modification.

It is well known that the earlier theories of electric attraction and repulsion were based upon the assumption of an effluvium or emanation which was supposed to be given off by some bodies when rubbed by other bodies, and which was generally supposed to return to its origin when the rubbing ceased. This notion seems to have been original with Gilbert, who believed that bodies are held to the earth by some kind of a force exerted by the atmosphere, "the earth's effluvium," and who accordingly attributed an analogous, though much more rarefied, effluvium to the electrified amber.⁷²

Gilbert knew nothing of electric repulsion, and when this phenomenon was first observed by Cabeus, in 1629,⁷³ it was attributed to vortex currents set up in the air by the emanation. It was finally recognized as a true electrical force by Von Guericke, about the middle of the seventeenth century.

This discovery seemed to double the difficulty of finding an explanation for electrical phenomena, and when in 1733 Du Fay discovered the two kinds of electrification, which seemed to make necessary two kinds of emanations, the problem became still more complex.

The first simplification was proposed by Franklin, and by Watson, in England, who assumed a single electric fluid, the particles of which are self-repellent, but which attract the particles of material bodies. Franklin attempted to show how all the electrical phenomena known in his day could be explained on this assumption of a single electric fluid. The earth was assumed to contain a common stock of this fluid, which is distributed throughout the earth and all bodies on its surface. So long as a body has its proportional share of this fluid it shows none of the properties which distinguish electrified bodies. *Certain bodies have the capacity*

⁷² Gilbert, "De Magnete," Mottelay's translation, p. 92.

⁷³ Cabeus, "Philosophia Magnetica," Chap. XXI, p. 154.

of taking some of this fluid from other bodies when the two are rubbed together.⁷⁴ Then one acquires an excess over the normal supply and the other is left with a deficiency. Franklin indicated these two states of electrification as the + and — conditions. Two bodies in the same condition, either + or —, then repel each other, while two bodies in the opposite state attract each other.

Franklin does not undertake to *explain* this attraction or repulsion, but merely calls attention to the phenomenon. For this reason he is sometimes said to have believed in the possibility of attraction at a distance.

Meanwhile, the notion that an electric attraction or repulsion was due to an atmosphere or effluvium emitted by the rubbed body was losing ground. Aepinus showed that a condenser with only the air between its plates may take a very high charge while the plates are close together, and he reasoned from this that air, as well as other insulators, is impervious to the electric fluid and, accordingly, that there cannot be an atmosphere of the electric fluid surrounding a charged body in air.

Professor Whittaker, in speaking of this work of Aepinus, says:⁷⁵

The theory of effluvia was finally overthrown, and replaced by that of action at a distance, by the labors of one of Franklin's continental followers, Francis Ulrich Theodore Aepinus.

This statement of Professor Whittaker seems to need modification, since Aepinus, himself, says:⁷⁶

I do not approve of the doctrine which assumes the possibility of action at a distance, for I hold as an indisputable axiom the statement that a body cannot act at a place where it is not; and if it should ever be proved that a certain attraction or repulsion does not altogether depend upon an external pressure or an internal impulse, then I think we have been reduced to such a position that we are compelled to conclude that motions of this kind are not produced by physical force, but by spirits or other beings, as to which I cannot be induced to believe that this idea has any foundation in the world.

It would seem from this that while Professor Whittaker may regard action at a distance as a necessary deduction from Aepinus's rejection of the theory of an electric atmosphere, Aepinus, himself, did not so understand it. A necessary inference from the expression of belief just quoted would seem to be that Aepinus looked upon electric attraction and repulsion as due to an external pressure exerted upon the electrified bodies by some physical medium other than the electric fluid.

⁷⁴ This seems to be the first recognition of the different affinities of different bodies for electricity.

⁷⁵ "History of the Theories of Aether and Electricity," p. 48.

⁷⁶ "Tentamen Theoriae Electricitatis et Magnetismi": St. Petersburg, 1759, p. 7. Translated for the writer by Professor Jefferson Elmore.

This point of view would seem to make him rather the precursor of the later ether theory of electric attraction than that of action at a distance. This inference seems strengthened by the fact that Aepinus expressed a firm belief that the electric fluid is different from both the substance of material bodies and the ether of space.

This notion of a pressure exerted upon the electric fluid by some surrounding medium is brought out much more clearly in the writings of Cavendish only a few years later. Cavendish read a paper before the Royal Society in 1771,⁷⁷ in which he says that since the paper was written he finds that Aepinus had made use of nearly the same hypothesis in 1759.

Cavendish says in describing his hypothesis:⁷⁸

There is a substance, which I call the electric fluid, the particles of which repel each other and attract the particles of all other matter with a force inversely as some less power of the distance than the cube; the particles of all other matter also repel each other and attract those of the electric fluid, with a force varying according to the same power of the distances. Or, to express it more concisely, if you look upon the electric fluid as matter of a contrary kind to other matter, the particles of all matter, both those of the electric fluid and of other matter, repel particles of the same kind, and attract those of a contrary kind, with a force inversely as some less power of the distance than the cube.

In his paper on "Thoughts Concerning Electricity"⁷⁹ Cavendish says:

Def. 1. When the electric fluid within any body is more compressed than in its natural state, I call that body positively electrified. When it is less compressed, I call the body negatively electrified.⁸⁰

It is plain from what has been said here that if any number of conducting bodies be joined by conductors and one of the bodies be positively electrified, all the others must be so too.

Def. 2. When any body contains more of the electrical fluid than it does in its natural state, I call it overcharged. When it contains less, I call it undercharged.

Hyp. 1st. Every body overcharged with electricity repels an overcharged body, and attracts an undercharged one.

Hyp. 2d. Every undercharged body attracts an overcharged body, and repels an undercharged one.

Hyp. 3d. Whenever any body overcharged with electricity is brought near any other body, it makes it less able to contain electricity than before.

⁷⁷ "An Attempt to Explain Some of the Principal Phaenomena of Electricity by Means of an Elastic Fluid," *Philosophical Transactions*, 41, 584-672.

⁷⁸ "Electrical Researches," p. 3.

⁷⁹ "Electrical Researches," p. 96.

⁸⁰ Cavendish explains elsewhere that by "compressed" he means under more than the normal external pressure, but he does not mean that the volume of the fluid is necessarily reduced.

Hyp. 4th. Whenever an undercharged body is brought near another it makes it more able to contain electricity.

* * * * *

Cor. II. If two bodies, both perfectly insulated, so that no electricity can escape from them, be positively electrified and then brought near to each other, as they are both overcharged, they will each, by the action of the other upon it, be rendered less capable of containing electricity, therefore, as no electricity can escape from them, the fluid within them will be rendered more compressed, just as air included within a bottle will become more compressed either by heating the air or by squeezing the bottle into less compass; but it is evident that the bodies will remain just as much overcharged as before.

* * * * *

Cor. V. If a body overcharged with electricity be brought near a body not electrified, and not insulated, part of the electric fluid will be driven out of this body, and it will become undercharged.

But if the body be insulated, as in that case the electric fluid cannot escape from it, it will not become undercharged, but the electric fluid within it will be more compressed than in its natural state, *id est*, the body will become positively electrified, and will remain so as long as the overcharged body remains near it, but will be restored to its natural state as soon as the overcharged body is taken away, provided no electricity has escaped during the meantime.

* * * * *

Hyp. 5th. It seems reasonable to suppose that *when the electric fluid within any body is more compressed than it is in the air surrounding it, it will run out of that body, and when it is less compressed it will run into the body.*⁸¹

It will be seen from the above quotations that Cavendish had an electrical theory very different from that of any of his predecessors, and that he undertook to explain the phenomena of electrostatics in terms of a pressure, or repulsion, instead of in terms of an attraction, as was later attempted by Faraday, and as is still attempted in the current electrical theory. From the quotations so far given, it might be inferred that Cavendish sought the cause of this pressure in some kind of an elastic stress in a surrounding medium, but he does not declare his disbelief in the possibility of action at a distance, as did Aepinus, and he frequently speaks of the repulsion of the electrical particles as extending to considerable distances. Thus he says on page 103 of "Electrical Researches":

If the electric fluid be diffused uniformly through all bodies not appearing electrical and the repulsion of its particles extends to considerable distances, it is plain that the consequences are such as are here described; but how far that supposition will agree with experiment I am in doubt.

Unfortunately, the work of Cavendish in electricity was not given to the world for one hundred years after its completion, and his original discoveries had to be remade by others; while his still more original interpretation of electrical phenomena has never received the serious consideration which it deserves. It was given to the world at a time when the

⁸¹ Italics mine. —F. S.

epoch-making discoveries of Faraday had dazzled the eyes of physical philosophers to such an extent that no other theory than that of Faraday could hope to receive consideration. Now, since the fundamental assumptions of the Faraday theory of electric attraction and repulsion are known to be incorrect, while those of Cavendish are still in accord with the facts as we know them, it seems probable that Cavendish's interpretations will receive the consideration to which they seem entitled.

The especial reason for dwelling upon the theories of Cavendish at this time is to call attention to the fact that he made repulsion, instead of attraction, the fundamental phenomenon, and that he thought of the electric fluid in a charged body as always under pressure due to a surrounding medium and as, in turn, exerting a pressure upon this medium.

Dr. Thomas Young was apparently the first to suggest definitely that electric attractions and repulsions are due to pressure in an elastic medium. In his "Lectures on Natural Philosophy," published in 1807, Young says:

It must be confessed that the whole science of electricity is yet in a very imperfect state: we know little or nothing of the intimate nature of the substances and actions concerned in it: and we can never foresee, without previous experiment, where or how it will be excited. We are wholly ignorant of the constitution of bodies, by which they become possessed of different conducting powers; and we have only been able to draw some general conclusions respecting the distribution and equilibrium of the supposed electric fluid, from the laws of the attractions and repulsions that it appears to exert: there seems to be some reason to suspect from the phenomena of cohesion and repulsion, that the pressure of an elastic medium is concerned in the origin of these forces; and if such a medium exists, it is perhaps nearly related to the electrical fluid.

It should be noticed that while Young suggests that attraction and repulsion are due to the pressure of an elastic medium, he does not mention the luminiferous ether. At this time, in fact, the luminiferous ether was just coming to be recognized through Young's own work on interference of light.

The one important discovery in electrostatics between the times of Cavendish and of Young was the discovery of contact electrification by Bennett. Meanwhile, the quantitative studies in electricity which resulted largely from the publications of Coulomb gave the first opportunity for the application of mathematics to the study of electricity, and since the notion of action at a distance lends itself to mathematical analysis much more readily than does the idea of elastic stresses in a medium, the earlier mathematical theory of electricity was based wholly upon this concept. Since there were then, as now, many more mathematicians than physical philosophers in the world, the question "How much?" came to be considered more important than the question "How?", and the possibility or impossibility of action at a distance ceased to receive consideration until it was revived by the discoveries of Faraday.

Faraday's most important discoveries regarding the phenomena of electrification were his proofs of the perfect equality in magnitude of the inducing and induced charges in all cases, his proof that electrical induction might sometimes act in curved lines (as he states it) and hence could not be due to the action of force at a distance, as such action would necessarily be rectilinear, and finally, in 1837, his discovery of specific inductive capacity. The first and the last named of these discoveries had previously been made by Cavendish.

Faraday's discovery of specific inductive capacity resulted from a determination of the distribution of an electric charge over two equal conductors when one of them was surrounded by air and the other by some other insulating medium.⁸² The apparatus used consisted of two brass balls 2.33 inches in diameter and exactly alike, mounted upon insulating supports concentrically inside of two similar hollow brass spheres of 3.57 inches internal diameter. The inner balls were carefully insulated from the outer hollow conductors, and the space between the two could be filled with air, or with some insulating liquid or solid. The outer hollow spheres were joined to earth.

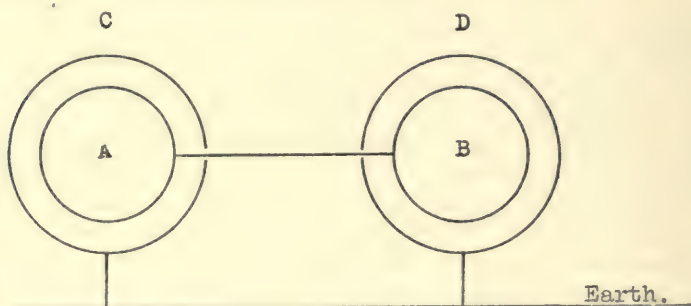


FIGURE 26. Faraday's Experiment on Specific Inductive Capacity.

Thus in the diagram in Figure 26 the inner spheres are indicated by *A* and *B*, the outer hollow spheres by *C* and *D*. *C* and *D* are joined to earth. If now *A* and *B* are connected by a wire and charged, then separated and the hollow spheres removed from around them, they are found to have equal charges.

The space between *A* and *C* was half filled with sulphur and *A* and *B* were then connected and charged. When the outer spheres and the sulphur were removed, *A* was found to have 2.24 times as great a charge as *B*. This was repeated, using glass, shellac and other substances instead of sulphur, with the same result, only with different values for the charge on *A*.

⁸² "Experimental Researches," paragraphs 1187-1294.

Faraday believed that the charges on A and B did not represent an increase or deficiency of the electric fluid, as had been believed by Franklin and his followers. In fact, Faraday did not believe in the necessity of any electric fluid at all. On the contrary, he believed the so-called charges upon A and B to be merely manifestations of some condition known as induction which had been produced in the medium between the inner and outer spheres. He says (Art. 1174, "Experimental Researches") :

The conclusion I have come to is, that non-conductors, as well as conductors, have never yet had an absolute and independent charge of one electricity communicated to them, and that to all appearance such state of matter is impossible.

Again (Arts. 1177 and 1178) :

Again, as far as experiment has proceeded, it appears, therefore, impossible either to evolve or to make disappear one electric force without equal and corresponding change in the other. It is also equally impossible to charge a portion of matter with one electric force independently of the other. Charge always implies *induction*, for it can in no instance be effected without; and also the presence of the *two* forms of power, equally at the moment of development and afterwards. There is no *absolute* charge of matter with one fluid; no latency of a single electricity. This, though a negative result, is an exceedingly important one, being probably the consequence of a natural impossibility, which will become clear to us when we understand the true condition and theory of the electric power.

The preceding considerations already point to the following conclusions: Bodies cannot be charged absolutely, but only relatively, and by a principle which is the same with that of *induction*. All *charge* is sustained by induction. All phenomena of *intensity* include the principle of induction. All *excitation* is dependent on or directly related to induction. All *currents* involve previous intensity and therefore previous induction. INDUCTION appears to be the essential function both in the first development and the consequent phenomena of electricity.

From this point of view, the so-called charges of A and B in the above experiment were merely manifestations of some condition known as induction in the medium between A and C and between B and D . If A assumed a larger proportion of the total electrification than B , it was because induction took place more freely between A and C than between B and D . Faraday accordingly said that sulphur had a greater capacity for electrical induction than air, and that if the inductive capacity of air were taken as one, the inductive capacity of sulphur would be greater than 2.24.

That this interpretation of the nature of electrification was entirely different from any which had preceded it was recognized by Faraday. Electrical theories previously proposed involved the existence of one or two electric fluids, but the Faraday theory does not involve the necessity of any electric fluid whatever. Faraday calls attention to this in a footnote to the article from which quotation has just been made. He says:

The theory of induction which I am stating does not pretend to decide whether electricity be a fluid or fluids, or a mere power or condition of recognized matter. That is a question which I may be induced to consider in the next or following series of these researches.

The great theoretical importance of the Faraday experiment arises from the fact that it showed that whether direct action at a distance is ever possible or not, electric attractions and repulsions are not due to such action, but necessarily to the direct action of one particle upon contiguous particles throughout the electric field. It may also be made to answer definitely the question whether the transference of the electric fluid (electrons) from one body to another is due to an attraction, as is held by the Faraday-Maxwell-Thomson theory, which has become our current theory, or whether it is due to a repulsion or pressure, as was believed by Cavendish.

Thus, in this experiment, when both the inner spheres, *A* and *B*, are surrounded with air and a charge is given to the wire which joins them, we know that half the charge flows to *A* and half to *B*. According to our current theory, these charges are drawn to *A* and *B* by the contraction of the medium between *A* and *C* and *B* and *D*, or, rather, by the contraction of lines or filaments extending through this medium from the inner to the outer spheres. According to the Cavendish theory, the charges flow to *A* and *B* because there is a less external pressure upon the electric fluid in *A* and *B* than upon the fluid in the conductor from which they are being charged. The pressure upon the electric fluid in *A* and *B* is necessarily exerted by the medium surrounding them and between them and their outer conductors. Since the same medium surrounds both, and since the conditions are symmetrical over both, both will require the same charge in order to exert the same pressure upon this surrounding medium. This is regardless of whether the electrons flow into, or out of, *A* and *B* during the charging process.

If the space between *A* and *C* be half filled with sulphur, *A* will take more than twice as great a charge as *B* when their charges are in equilibrium with each other and with the charge in the conductor from which they are being electrified. If these charges are drawn in by the contraction of lines of force between the inner and outer spheres, then an electric attraction between two given charges must be greater through sulphur than through air. If, on the contrary, the electric fluid flows into *A* and *B* under the impulse of an external pressure, it will continue to flow into them until the external pressure upon it is equalized over all the connected conductors. Since more flows into the sphere which is partly surrounded by sulphur than into the one wholly surrounded by air, it must follow that the external pressure exerted upon a given charge

in a conductor when the conductor is surrounded by sulphur is less than when it is surrounded by air.

We can easily test the first of these hypotheses, and we know that the attraction between two given charges is about one-third as great through sulphur as through air. Hence, if the charges had been drawn into *A* and *B* by an attraction through the surrounding medium (by lines or tubes of force stretching across from the inner to the outer conductor, as our current theory has it) a greater charge should be drawn into *B* than into *A*.

This is not saying that Faraday drew a wrong conclusion from his premises. As long as there was nothing but induction to consider, it was logical to assume that the greater induction took place around the larger charge, as, indeed, it does. But Faraday's theory was devised to explain electrification without any electric fluid whatever. Now, that the electric fluid has been definitely identified and we know which way it flows when one body is electrified from another, Faraday's classical experiment may be made to furnish the proof that this fluid flows from a region of higher to a region of lower pressure, as does any other fluid, and as it was supposed by Cavendish to flow.

In 1873 Maxwell published the first edition of his "Electricity and Magnetism," which brought some of the fundamental ideas of Faraday into a position of prominence in the English-speaking world which they have since held. Maxwell undertook to show that the quantitative laws of Electricity and Magnetism which had been put into mathematical form on the assumption of forces acting at a distance could also be put into mathematical form on the basis of Faraday's hypothesis of stresses in an elastic medium. By making a number of unverifiable assumptions regarding the nature of the medium in which induction was assumed to take place, Maxwell partially, but not wholly, accomplished his undertaking. His greatest contribution to electrical theory was the identification of the elastic medium in which induction takes place with the luminiferous ether and the recognition of the electrical nature of radiation.

Maxwell specifies the condition of induction which he assumed to account for electrical attraction as follows:

At every point of the medium there is a state of stress such that there is a tension along the lines of force and pressure in all directions at right angles to these lines, the numerical magnitude of the pressure being equal to that of the tension, and both varying as the square of the resultant force at that point.

Maxwell does not claim that this explains the phenomena of induction. It only describes the condition within the medium which it seemed to him necessary to assume in order to express Faraday's concept of electrical attraction in mathematical terms. He says in this connection:

It must be carefully borne in mind that we have made only one step in the theory of the action of the medium. We have supposed it to be in a state of stress, but we have not in any way accounted for this stress, or explained how it is maintained. This step, however, seems to me to be an important one, as it explains by the action of the consecutive parts of the medium, phenomena which were formerly supposed to be explicable only by direct action at a distance.

This is, of course, equivalent to saying that he knows of no reason why there should be such tension along the lines of force, but unless it exists he does not see how one electric charge can be pulled toward another by means of the ether. Evidently, if the displacement of electricity within conductors is due to a pressure, rather than to an attraction, there is no reason for assuming a contraction of the ether as the cause of the attraction.

If we agree with Larmor that according to any ether theory static electric attraction must be conveyed by elastic action through the ether, and that an electric field must be a field of elastic strain in the ether, and no one has yet thought of any other way of explaining electric attractions and repulsions, we have ready all the elements for a complete theory of static electrification.

It is a fundamental characteristic of elastic stress that the particles of the substance react to an external force in such a way as to tend to distribute the stress uniformly throughout the body. The reaction of the particles of the substance to the deforming stress is taken as the measure of its elasticity.

If a stress be set up in an unbounded elastic medium, the stress will be diffused throughout the whole medium. If several similar centers of stress exist simultaneously in such a medium, the elastic reaction of the medium upon these centers of stress will tend to distribute them uniformly throughout the medium; or in an unbounded medium it will tend to cause them to move apart continually. If such centers of stress are free to move about in the medium, they will separate. Since electric particles move with perfect freedom in the ether, *if they are centers of strain of any kind whatsoever, and if the ether reacts to this strain like an elastic material body, electrons will repel each other, and no further explanation of the fundamental phenomena of repulsion is required or can be given.*

If the ether elasticity within conductors be greater than outside in the free ether, then an electric particle in the bounding surface of a conductor in the free ether will meet with a greater resistance in moving into the conductor than in moving outward into the free ether. If, on the other hand, the ether elasticity be less in conductors than in free ether, an electron in the bounding surface of a conductor will be under

a greater pressure on the side of the free ether than on the side of the conductor. Such an electron will be hindered in escaping from the conductor by an external force due to the greater elasticity of the ether outside than inside the conductor.

It is well known that the elastic force of repulsion is less in all material media than in the free ether, hence charges upon the surface of conductors are held there by the elastic force of the external ether.

This answers a question which was long a puzzle to physicists, and which seems to have been given up as insoluble in our current electrical theory, viz., How may an electric charge upon a conductor be retained by the conductor while it is attracted by an external charge?

It was first assumed by Franklin that the particles of electric fluid attract the particles of matter while they repel each other. Then it was shown that if this were the case the electric attraction by a body of a given charge, or, in other words, the electric capacity of a body, should depend upon its mass, whereas, it was found that the electric capacity of a hollow sphere was exactly equal to that of a solid sphere of the same size.

When the two-fluid theory came into prominence the same difficulty applied to it, hence it came to be accepted as a principle of this theory that no attraction whatever exists between either of the electric fluids and the particles of matter. Electric attractions and repulsions were only between the electric fluids themselves.

But if this be the case, how may two bodies be pulled together by electric attraction? Why are the electric fluids not drawn away from the bodies by their mutual attraction?

Some of the answers which were proposed to this question are very amusing from our present point of view. Thus Dr. Thomas Thomson, in his work entitled "Outlines of the Sciences of Heat and Electricity," published in 1830, asks and answers this question as follows:

But if there be no affinity or attraction between electricity and matter, it may appear, at first sight, difficult to account for the fact that when bodies are excited, that is, contain a superabundance of electricity, they *attract* or *repel* each other with forces varying inversely as the square of the distance; bodies having the same kind of electricity repelling, and those having different kinds attracting each other. But this apparent difficulty admits of a very simple explanation.

If we suppose two excited and insulated spheres placed at a small distance from each other, it is obvious that the only forces which can occasion the motion of the bodies, are the mutual attraction or repulsion of the fluid in the one, to the fluid in the other. For the repulsions exercised by the particles of fluid in each body on one another, can have no effect in producing a motion in the center of gravity of either body. If the two spheres consist of non-conducting matter, the unknown power which gives them the non-conducting property, will prevent the escape of the electricity from each. Therefore the mutual attractions and

repulsions of the fluids, as they cannot escape from the matter, may be supposed to carry the matter along with them, and thus to cause the globes to approach or recede, according as they are charged with different kinds of electricity, or with the same kind.

When an excited conducting body is insulated the superinduced electricity forms a coating on its surface, and (if we suppose the body spherical) the thickness of this coating will be everywhere the same. This electricity presses upon the ambient air, which prevents it from making its escape. The excited sphere, in consequence of this action of the electricity, which is proportional to the square of its thickness, will be less pressed upon by the surrounding atmosphere than if it were not excited. But as the pressure, though diminished, is everywhere equal, there will be no tendency of the sphere to move from its place. Let us suppose the conducting sphere to be charged with positive electricity, and let us conceive a mass of sealing wax or gum lac, charged negatively, to approach it, a portion of the combined electricity natural to the sphere, will be decomposed. The positive portion will accumulate on the surface of the sphere next the mass of sealing wax, being attracted by its negative electricity. The superabundant positive electricity already in the sphere will accumulate at the same surface for the same reason. While the decomposed negative electricity will accumulate at the opposite surface of the sphere, being repelled by the negative electricity of the sealing wax. Thus the coating of electricity next the sealing wax will become thicker than before, while the coating at the greatest distance will become thinner. Hence the electricity in the part of the sphere next the sealing wax will press more upon the air than before, while the air will press more than before upon that surface of the sphere which is farthest from the sealing wax. Both of these pressures have a tendency to cause the sphere to move towards the sealing wax, and if the weight of the sphere be sufficiently small it will move accordingly.

It is difficult to see how anyone with even an elementary acquaintance with the mechanics of Newton could call this a very simple explanation, or, in fact, could be hypnotized into thinking it any explanation at all, but Dr. Thomson evidently took it seriously, and he proceeded immediately after the above quotation to put it into mathematical form. Dr. Thomson was a very eminent scientific man, Professor of Chemistry in the University of Glasgow, Fellow of the Royal Societies of London and Edinburgh, and member of most of the learned societies of Great Britain and the Continent. It is accordingly probable that this represents the best explanation at that time available of this difficult electrical problem.

De la Rive, in his great treatise on "Electricity", published twenty-three years later, is still wrestling with this problem. He still seemed satisfied with the explanation which Thomson had given with regard to insulators, that while their particles could have no attraction for electricity, still "The unknown power which gives them the non-conducting property will prevent the escape of electricity from each," and accordingly that they may be pulled together by the attraction of their electric fluids; but in the meantime Becquerel, Sir W. Snow Harris and others

had repeated the discovery made one hundred years before by Hauksbee and Stephen Gray, that electric attraction and repulsion may take place in the best air-pump vacuum. De la Rive, referring to this experiment, says:

Sir W. Snow Harris has observed that the attractions and repulsions between electrised bodies take place in vacuo as they do in air; a further proof of the error we should commit in admitting atmospheric pressure to play a part in the phenomena. This fact, on the other hand, is very well explained by admitting that the electricities are retained, in the portions of the surfaces where they are distributed, by the insulating effect of the film of air that remains adjacent, and in no degree by atmospheric pressure: once retained at the surface by this cause, as they would have been by a coating of varnish, they are no longer able to obey their mutual attraction or repulsion, except by drawing with them the bodies themselves, if their mass is not too great. This explanation, even though it should not be based upon observations made in vacuo, would seem to us in every case preferable to that in which atmospheric pressure is made to intervene; this intervention being implicitly founded on a purely hypothetical idea, namely, that electricity is a fluid of the same kind, and about the same tenuity as air and gases.

Further, while still believing that the electric effects observed in vacuo, as well as others no less curious, of which we shall speak hereafter, are due to the film of air that remains adhering to the surface of bodies, we by no means wish to pretend that conducting bodies have not for themselves the property of preserving, or rather of *coercing* on their surface a certain dose of electricity, feeble, it is true, but nevertheless sensible.

When the Faraday theory came into general acceptance this question had no further significance, since from Faraday's point of view there was no electric fluid upon a charged conductor; but with the identification of the electric fluid by J. J. Thomson and his students this question again became pertinent.

Since in the current Maxwell-Thomson theory attraction is still the fundamental phenomenon, and since the lines or tubes of force are supposed to extend from any charged conductor to an opposite charge upon another body, the only force acting upon an electrical charge is one pulling it away from the conductor upon which it is located, and no provision whatever is made in this theory for holding it back. It would accordingly seem that the assumption of a pressure upon the particles of electricity, somewhat as was assumed by Cavendish, is as necessary for explaining the retention of electric charges by material bodies, whether conductors or non-conductors, as it is for explaining the phenomena of Faraday's famous specific inductive capacity experiment.

FUNDAMENTAL ASSUMPTIONS OF ELECTRIC THEORY

We accordingly have the following fundamental postulates by which to explain electrical phenomena:

1. An elastic ether, pervading all known space, passing between

and perhaps through the atoms and molecules of all bodies; its electrical elasticity being less between the atoms and molecules of bodies than in free space.

From the transverse character of light waves and electric waves in the ether, we regard its elasticity as analogous to rigidity in material bodies. We have no data upon its compressional elasticity, but it is generally regarded as very great.

2. We have electrons which, whatever their nature, act as centers of strain in this medium, and on this account, and by virtue of the elastic reaction of the ether to this strain, repel each other. When in the free ether and at a distance from material bodies they appear to have perfect freedom of movement.

3. We have the earth containing a sufficient number of electrons, both combined and free, to produce a field of great ether strain around it.

4. We have the atoms of material bodies, which also contain electrons, but which seem to contain particles of a substance different from electricity. Since the atomic mass seems to be determined chiefly by this part of the atom, and since mass is the one unchanging characteristic of material bodies, these particles may be called the material sub-atoms.

We also know that each of these material sub-atoms requires a different number of electrons to bring its electrical pressure up to the normal pressure in the ether of the earth's field (to neutralize its positive charge), hence that it has a *characteristic positive charge*, and that the greater this characteristic positive charge the less the electric elasticity of the adjacent ether.

5. It is known from experiment that the elastic stress around a charged spherical conductor falls off with the square of the distance from the center of the sphere. This being true, the ether stress about a sphere as large as the earth would be of nearly the same intensity on all sides of a small body. That is, the pressure upon an electric charge in the earth's field is nearly of the nature of a hydrostatic pressure. (We have seen that in the atmosphere four miles above the earth's surface it differs from a hydrostatic pressure by only eight or nine volts per meter.) Within hollow conductors upon the earth the pressure upon an electric charge will be a true hydrostatic pressure.

It has already been shown by the writer⁸³ that the above postulates are sufficient for providing a reasonable explanation of all known electrical phenomena except the phenomena of electromagnetism. No electric theory has yet given any explanation whatever of this class of phenomena.

⁸³ "A Physical Theory of Electrification," Leland Stanford Junior University Publications, Stanford University, California, 1911.

LIST OF TABLES

| TABLE | PAGE |
|--|------|
| I. Mobility of Ions | 16 |
| II. Ionic Volumes and Ionic Speeds of Alkali Metals | 18 |
| III. Relative Ionic Charges | 19 |
| IV. Relation of Contact Electromotive Series to Cohesion..... | 21 |
| V. Ionic Charges and Compressibility | 23 |
| Va. Expansion Coefficients and Ionic Charges | 24 |
| VI. Melting Points and Ionic Charges | 25 |
| VII. Relation of Heydweiller's <i>Ionenmodulus</i> to Ionic Charges..... | 26 |
| VIII. Molecular Charges and Melting Points | 27 |
| IX. Ionic Charges and Boiling Points | 28 |
| X. Molecular Charges and Boiling Points | 30 |
| XI. Ratio of Temperatures of Equal Ammonia Pressures over Am- moniated Salts to the Charge of the Negative Ion..... | 31 |
| XII. Molecular Charges and Critical Temperatures | 33 |
| XIII. Atomic Heat of Fusion and Ionic Charge | 33 |
| XIV. Kleeman's Cohesion Constant and Ionic Charges | 34 |
| XV. Lowering of Surface Tension of Mercury and Ionic Charge..... | 35 |
| XVI. Relation of Densities to Molecular Charges | 36 |
| XVII. Heats of Formation and Products of Ionic Charges | 37 |
| XVIII. Molecular Heats of Formation and Molecular Charges | 40 |
| XIX. Ionization Constants | 41 |
| XX. Molecular Charges and Solubilities | 44 |
| XXI. Solubility and Charge of Negative Ion | 44 |
| XXII. Solubility of CO ₂ in Benzole and its Derivatives | 45 |
| XXIII. Expansion of Dissolved Salts compared with their Molecular Charges | 46 |
| XXIV. Serial Numbers and Atomic Charges..... | 50 |
| XXV. Serial Numbers and Cohesion..... | 52 |
| XXVI. Charges of Ions from Hot Metals..... | 55 |
| XXVII. The Convergence Charge of the Balmer Series..... | 65 |
| XXVIII. The Convergence Charge of the Pickering Series..... | 67 |
| XXIX. Values of $2e$ from the Principal Series of Hydrogen..... | 68 |
| XXX. Values of $2e$ from the Ritz-Lyman Series..... | 68 |
| XXXI. Nuclear Charges from K -Radiation..... | 73 |
| XXXII. Difference in K - and L -Radiation Charges | 75 |
| XXXIII. Wave-Lengths of L - γ_3 Lines | 76 |
| XXXIV. Comparison of the Speeds of β -Rays with the Orbital Speeds of Electrons in γ -Radiation | 79 |
| XXXV. Charges of Electrolytic Ions Calculated from Ionic Mobilities and from Atomic Numbers | 81 |
| XXXVI. Ionic Charges Calculated from Nuclear Charges..... | 82 |
| XXXVII. Specific Inductive Capacities of Metals..... | 110 |

130

LIST OF FIGURES

| FIGURE | PAGE |
|---|------|
| 1. Relation of Compressibility to Ionic Charge..... | 23 |
| 2. Relation Between Expansion Coefficients and Ionic Charges | 24 |
| 3. Relation Between Melting Points and Molecular Charges..... | 28 |
| 4. Relation of Vapor Pressure to Ionic Charges..... | 29 |
| 5. Relation of Molecular Charges to Boiling Points | 30 |
| 6. Ratio of Temperatures of Equal Ammonia Pressure over Ammoniacated Salts to the Charge of the Negative Ion..... | 31 |
| 7. Relation of Critical Temperature to Ionic Charge..... | 32 |
| 8. Relation of Density to Molecular Charge..... | 36 |
| 9. Heats of Formation and Products of Ionic Charges..... | 37 |
| 10. Relation of Heats of Formation to Charges of Negative Ion..... | 38 |
| 11. Relation of Molecular Heats of Formation to Molecular Charges..... | 40 |
| 12. Relation of Ionization of Gases to Ionic Charges..... | 41 |
| 13. Relation of Heats of Ionization to Ionic Charges..... | 42 |
| 14. Decrease of Solubility of CO_2 in Benzole Derivatives with an Increase in the Negative Charge of the Substituted Ion..... | 45 |
| 15. Relation of Expansion of Salts Dissolved in Water to Their Molecular Charges | 46 |
| 16. Relation Between the Serial Numbers and the Atomic Charges of Monova- lent Elements | 51 |
| 17. Relation of Critical Temperature to the Serial Numbers of the Elements.... | 52 |
| 18. Relation of Sutherland's Cohesion Constant to the Serial Numbers of the Elements | 53 |
| 19. Relation of the Cohesion Constant " a " to the Serial Numbers of the Atoms.. | 54 |
| 20. Relation of the Charges of Ions from Hot Metals to the Serial Numbers of the Elements | 56 |
| 21. Relation Between Heydweiller's Atomic Radii and Radii from Einstein's Photoelectric Equation | 63 |
| 22. Relation of Cube Root of Atomic Volume to Radii Calculated from Ein- stein's Equation | 63 |
| 23. Relation of Nuclear Charges to Ionic Charges..... | 82 |
| 24. Relation of Nuclear Charges to Charges of Ions from Hot Metals..... | 83 |
| 25. Induction Due to Natural Charges of Metals..... | 91 |
| 26. Faraday's Experiment on Specific Inductive Capacity..... | 120 |

132

UNIVERSITY SERIES

- THE PRONOUN OF ADDRESS IN ENGLISH LITERATURE OF THE THIRTEENTH CENTURY. Arthur Garfield Kennedy, Instructor in English Philology. 91 pp. 1915. Price \$1.00.
- THE ANOPLURA AND MALLOPHAGA OF NORTH AMERICAN MAMMALS. Vernon Lyman Kellogg, Professor of Entomology, and Gordon Floyd Ferris. 74 pp., 18 text figures, 8 plates. 1915. Price 75c.
- THE FLÜGEL MEMORIAL VOLUME. Papers by Ewald Flügel, late Professor of English Philology, his Colleagues and Students. 232 pp. 1916. Price \$1.50.
- THE SESAMOID ARTICULAR: A BONE IN THE MANDIBLE OF FISHES. Edwin Chapin Starks, Assistant Professor of Zoology. 40 pp., 15 text figures. 1916. Price 50c.
- A STUDY OF GERMAN VERBS COMPOUNDED WITH AUS, EIN, ETC., AS CONTRASTED WITH THOSE COMPOUNDED WITH HERAUS, HINAUS, HEREIN, HINEIN, ETC. Charles Reining, Instructor in German. 142 pp. 1916. Price \$1.00.
- THE PATHOLOGY OF NEPHRITIS. William Ophüls, Professor of Pathology. 103 pp., 64 text figures and plates. 1916. Price \$1.00.
- BONE AND JOINT STUDIES, I. Leonard W. Ely, Associate Professor of Surgery, and John Francis Cowan, Assistant Professor of Surgery. 139 pp., 41 text figures and plates. 1916. Price \$1.00.
- A STUDY OF THE MAGMATIC SULFID ORES. C. F. Tolman, Jr., Associate Professor of Economic Geology, and Austin F. Rogers, Associate Professor of Mineralogy and Petrography. 76 pp., 7 text figures, 20 plates. 1916. Price \$1.00.
- THE GENERA OF FISHES, FROM LINNÆUS TO CUVIER, 1758 TO 1833 (SEVENTY-FIVE YEARS), WITH THE ACCEPTED TYPE OF EACH. David Starr Jordan, Chancellor Emeritus. 161 pp. 1917. Price \$1.00.
- THE USE OF YE IN THE FUNCTION OF THOU IN MIDDLE ENGLISH LITERATURE FROM MS. AUCHINLECK TO MS. VERNON. Russell Osborne Stidston, late Acting Instructor in English. 95 pp. 1917. Price 75c.
- EMERSON: A STATEMENT OF NEW ENGLAND TRANSCENDENTALISM AS EXPRESSED IN THE PHILOSOPHY OF ITS CHIEF EXPONENT. Henry David Gray, Associate Professor of English. 110 pp. 1917. Price 75c.
- THE NEO-CLASSIC MOVEMENT IN SPAIN DURING THE XVIII CENTURY. Robert E. Pellissier, late Assistant Professor of Romanic Languages. 187 pp. 1918. Price \$1.00.
- THE ORIGINAL VERSION OF "LOVE'S LABOUR'S LOST," WITH A CONJECTURE AS TO "LOVE'S LABOUR'S WON." Henry David Gray, Associate Professor of English. 55 pp. 1918. Price 75c.
- THE CALIFORNIA SPECIES OF MEALY BUGS. Gordon Floyd Ferris, Instructor in Entomology. 78 pp., 16 text figures, 3 plates. 1918. Price \$1.00.
- LIBERAL AND VOCATIONAL STUDIES IN THE COLLEGE. Henry Waldgrave Stuart, Professor of Philosophy. 72 pp. 1918. Price 75c.
- THE DERIVATION OF THE FLORA OF HAWAII. Douglas Houghton Campbell, Professor of Botany. 34 pp. 1919. Price 50c.
- A CONTRIBUTION TO THE KNOWLEDGE OF THE COCCIDAE OF SOUTHWESTERN UNITED STATES. Gordon Floyd Ferris, Instructor in Entomology. 68 pp., 38 text figures. 1919. Price \$1.00.
- THE GENERA OF FISHES, PART II, FROM AGASSIZ TO BLEEKER, 1833 TO 1858 (TWENTY-SIX YEARS), WITH THE ACCEPTED TYPE OF EACH. David Starr Jordan, Chancellor Emeritus. Pp. 163-284, with Index. 1919. Price \$1.00.
- THE ELECTRICAL CHARGES OF ATOMS AND IONS. Fernando Sanford, Professor of Physics. 130 pp. 1919. Price \$1.00.

Physics
Elect.
S.

177130

Author Sanford, Fernando

Title The electrical charges of atoms and ions.

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
Under Pat. "Ref. Index File"
Made by LIBRARY BUREAU

